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Building high-coverage monolayers of covalently bound magnetic nanoparticles

Mackenzie G. Williams, Andrew V. Teplyakov*

Department of Chemistry and Biochemistry, University of Delaware, Newark, DE 19716, USA

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ABSTRACT

This work presents an approach for producing a high-coverage single monolayer of magnetic nanoparticles using "click chemistry" between complementarily functionalized nanoparticles and a flat substrate. This method highlights essential aspects of the functionalization scheme for substrate surface and nanoparticles to produce exceptionally high surface coverage without sacrificing selectivity or control over the layer produced. The deposition of one single layer of magnetic particles without agglomeration, over a large area, with a nearly 100% coverage is confirmed by electron microscopy. Spectroscopic techniques, supplemented by computational predictions, are used to interrogate the chemistry of the attachment and to confirm covalent binding, rather than attachment through self-assembly or weak van der Waals bonding. Density functional theory calculations for the surface intermediate of this copper-catalyzed process provide mechanistic insight into the effects of the functionalization scheme on surface coverage. Based on this analysis, it appears that steric limitations of the intermediate structure affect nanoparticle coverage on a flat solid substrate; however, this can be overcome by designing a functionalization scheme in such a way that the copper-based intermediate is formed on the spherical nanoparticles instead. This observation can be carried over to other approaches for creating highly controlled single- or multilayered nanostructures of a wide range of materials to result in high coverage and possibly, conformal filling.

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1. Introduction

The role of layered nanostructures has become increasingly prevalent in applications such as sensing [1], energy storage [2], photovoltaics [3], composite materials [4], spintronics [5], and biotechnology [6]. As a result, the importance of nanoscale surface control over these structures has become increasingly crucial. The introduction of specific properties, such as magnetism, to nanostructures has also attracted substantial interest because of the alteration of magnetic properties as these materials approach the nanoscale [7]. For example, Koh and Josephson give an overview of biosensing applications based on magnetic nanoparticles [8], and a perspective by Liou suggests that careful placing of magnetic nanoparticles at the point tip for magnetic force microscopy provides a superior performance compared to the more traditional materials, such as thin films [9]. A number of investigations have also been reported on the use of magnetic nanoparticles in magnetic tunnel junctions [10] and in materials exhibiting giant magnetoresistance [11]. In most of these cases, careful control of

the surface structure and conformal filling over high aspect-ratio features is essential. In some cases, such control can be attained through atomic layer deposition (ALD) and molecular layer deposition (MLD) methods [12]. Both approaches provide the ability to fine-tune a surface with atomic- and molecular-level precision but are limited to the size scale of their building blocks, requiring many deposition cycles before surface architectures can attain sizes larger than a few nanometers. Moreover, vacuum conditions are necessary for these methods. Alternatively, traditional self-assembly and layer-by-layer (LbL) growth methods can overcome these drawbacks by quickly producing layer thicknesses on the order of microns in a few deposition cycles [13]. Several reported LbL methods use nanoparticles or nanoparticle-incorporated materials to form thick layers and have been found to be useful for applications such as organic electronics [14], composite materials [4,15], and polymers [16]. Depending on the LbL approach used, however, the layers formed normally do not exhibit the conformal filling or sturdy attachment provided by ALD and MLD methods, nor does LbL growth guarantee a high degree of control over each individual layer formed.

In an approach fundamentally similar to ALD and MLD methods, the covalent attachment of mono- and multilayers of silica nanoparticles through the formation of a triazole ring has been

* Corresponding author.

E-mail address: andrewt@udel.edu (A.V. Teplyakov).

proposed previously [17–21]. The copper (I)-catalyzed formation of a triazole ring through an azide-alkyne Huisgen cycloaddition has been the focus of several studies aimed at building single and multiple layered nanostructures for a diverse range of applications. “Click chemistry” in general has become an umbrella term for high-yielding, selective reactions that can proceed quantitatively under innocuous conditions without producing undesirable byproducts [22]. This particular “click” reaction has been lauded for its formation of the relatively unreactive triazole ring and strong covalent attachment between the azide and alkyne moieties. Furthermore, the presence of the copper (I) catalyst enables this reaction to proceed very quickly.

This “click” reaction has been used to attach functionalized nanoparticles to a modified flat substrate to form a monolayer of covalently bound nanoparticles. Toulemon et al. has achieved this by attaching magnetic iron oxide nanoparticles to a gold substrate using a stirring procedure [18], and at an accelerated rate, by microwave irradiation [19]. Similarly, Upadhyay et al. has formed covalently bound nanoparticle layers using a variety of metallic, inorganic, and semi-conductor materials through the use of this “click” reaction in a dipping procedure [20]. In most of methods reported, nanoparticles are functionalized with azide groups and attached to an alkyne-terminated self-assembled monolayer. The opposite functionalization scheme is seldom reported; however, in one report, Kinge et al. modified a silica substrate with terminal azide groups and used 5-hexanoic acid and 6-amino-1-hexyne to functionalize iron oxide nanoparticles with alkyne groups [21]. Kinge et al. demonstrated that in addition to the more commonly used stirring and dipping procedures, the attachment could take place via microcontact printing methods [21].

These reports have outlined a straightforward system for the formation of these nanoparticle assemblies. However, the very high surface coverage, as well as the formation of only one single nanoparticle layer per deposition cycle that is necessary to ensure covalent bonding between each layer, have proven difficult to achieve until now. The method reported here highlights vital alterations that may provide insight into the parameters that affect coverage and complete monolayer formation. It is based on the nanoparticle layer deposition (NPLD) method that necessitates that the supporting solid substrate be functionalized with the azide moiety to produce a high-coverage nanoparticle monolayer [17]. Furthermore, it involves direct functionalization of substrate and particles with terminal complementary alkyl-azide and -alkyne groups, rather than more complicated structures. The surface coverage resulting from this method is very high compared to that of the monolayers in previously reported procedures. Additionally, the structures produced by this procedure are shown to consist of one single layer of nanoparticles, rather than clusters of agglomerated particles, which is significant because this chemistry must overcome intrinsic agglomeration of the magnetic material. A mechanistic insight into the reasoning for such a substantial improvement based on recent advanced understanding of the mechanism of “click chemistry” is offered. These modifications to the previously used procedure of forming nanoparticle layers via “click chemistry” are crucial for applications demanding very high surface coverage and offer a remarkable level of control over the formation of these layers.

2. Experimental

2.1. Alkyne functionalization of magnetic nanoparticles

To add alkyne functionality to the surface of the magnetic nanoparticles, 1 mL of 20 nm (18–22 nm) Fe_3O_4 nanoparticles dispersed in toluene (5 mg/mL, Sigma–Aldrich) and 1 mg of

10-undecynylphosphonic acid (>95%, Sikemia) were sonicated together for 20 min. The nanoparticles exchanged solvents by a series of washes in hexanes (Certified, Fisher Scientific) to produce 20 nm alkyne-functionalized magnetic nanoparticles dispersed in hexanes.

2.2. Azide modification of gold substrate

A pre-fabricated gold-coated wafer (1000 Å gold thickness on silicon wafer support with titanium adhesion layer, Sigma Aldrich) was cleaned in piranha solution (1:3 (by volume) hydrogen peroxide (30%, Fisher Scientific):concentrated sulfuric acid (98%, Fisher Scientific)) for five minutes, followed by cleaning in ultrapure water (18 M Ω cm, Quantum EX, EMD Millipore) for five minutes in order to remove organic contaminants. It was then rinsed with hydrochloric acid (37%, Fisher Scientific), water, ethanol (200 proof, Decon Labs), and dried in a stream of nitrogen. The substrate was added to a 1 mM ethanolic solution of 11-azido-undecanethiol (synthesized following a previously established procedure [23]) for 24 h, then was washed with ethanol, dichloromethane (>99.5%, Fisher Scientific), and water, and dried in a stream of nitrogen.

2.3. Monolayer formation of functionalized nanoparticles on substrate

To form a monolayer of magnetic nanoparticles on the azide-modified gold surface, 0.5 mL of alkyne-modified Fe_3O_4 nanoparticles in hexanes and 4:1 (by volume) dimethyl sulfoxide (>99%, Fisher Scientific):Millipore water were combined with catalytic amounts of copper sulfate pentahydrate (>99%, Sigma–Aldrich) and sodium ascorbate (>99%, Sigma–Aldrich). The “click” reaction was facilitated by one of two methods: either the solution was stirred with a mechanical stirrer (so as not to disturb the substrate) at room temperature for 48 h (based on the reaction time reported for similar systems [18]), or it was sonicated for 48 h, as indicated in the text. In both cases, the substrate was then washed with ethanol, dichloromethane, ethanol, and sonicated in ethanol for 30 min.

2.4. Characterization of monolayers

Scanning electron microscopy (SEM) was used to observe the nanoparticle monolayer formation following the “click” reaction with a Zeiss Auriga 60 SEM. Images were collected with an accelerating voltage of 5 kV and a working distance of 5.0 mm. Tapping mode atomic force microscopy (AFM) was used to confirm the presence of a single monolayer of nanoparticles on the substrate. The instrument used was a Veeco Multimode SPM with a Nanoscope V controller. Tap300Al-G tips (Budget Sensors) with a force constant of 40 N/m and a drive frequency of 300 kHz were used to obtain the images. The images were analyzed using Gwyddion software [24].

Single point attenuated total reflectance Fourier-transform infrared (ATR FT-IR) spectroscopy was performed on the azide-terminated surface and on the surface modified with the nanoparticle monolayer following the “click” reaction using an unmodified gold substrate sonically cleaned in ethanol as the background. The measurements were performed on a Bruker Optics (Billerica, MA) Vertex 70 FT-IR with a liquid nitrogen-cooled MCT detector and a Bruker Hyperion 2000 Microscope attachment, equipped with a dedicated single-point ATR attachment. Each spectrum was recorded as 64 scans at a resolution of 4 cm^{-1} over a range of 4000–600 cm^{-1} .

X-ray photoelectron spectroscopy (XPS) was performed on the samples to confirm covalent attachment of the nanoparticles to the surface through the “click” reaction using a Thermo Scientific K-Alpha+ equipped with an Al K α source ($h\nu = 1486.6 \text{ eV}$) at a take-off

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