Building High-Coverage Monolayers of Covalently-Bound Magnetic Nanoparticles

Mackenzie G. Williams¹ and Andrew V. Teplyakov^{1,*}

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

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.

Keywords: “click” reaction, high coverage, magnetic nanoparticle functionalization

*Corresponding author, Department of Chemistry and Biochemistry, University of Delaware, Newark, DE 19716; e-mail: andrewt@udel.edu, Ph.: (302) 831-1969, Fax: (302) 831-6335

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 has 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

1 [4,15], and polymers [16]. Depending on the LbL approach used however, the layers formed
2 normally do not exhibit the conformal filling or sturdy attachment provided by ALD and MLD
3 methods, nor does LbL growth guarantee a high degree of control over each individual layer
4 formed.

5 In an approach fundamentally similar to ALD and MLD methods, the covalent
6 attachment of mono- and multilayers of silica nanoparticles through the formation of a triazole
7 ring has been proposed previously [17–21]. The copper (I)-catalyzed formation of a triazole ring
8 through an azide-alkyne Huisgen cycloaddition has been the focus of several studies aimed at
9 building single and multiple layered nanostructures for a diverse range of applications. “Click
10 chemistry” in general has become an umbrella term for high-yielding, selective reactions that can
11 proceed quantitatively under innocuous conditions without producing undesirable byproducts
12 [22]. This particular “click” reaction has been lauded for its formation of the relatively
13 unreactive triazole ring and strong covalent attachment between the azide and alkyne moieties.
14 Furthermore, the presence of the copper (I) catalyst enables this reaction to proceed very quickly.

15 This “click” reaction has been used to attach functionalized nanoparticles to a modified
16 flat substrate to form a monolayer of covalently-bound nanoparticles. Toulemon *et al.* has
17 achieved this by attaching magnetic iron oxide nanoparticles to a gold substrate using a stirring
18 procedure [18], and at an accelerated rate, by microwave irradiation [19]. Similarly, Upadhyay *et*
19 *al.* has formed covalently-bound nanoparticle layers using a variety of metallic, inorganic, and
20 semi-conductor materials through the use of this “click” reaction in a dipping procedure [20]. In
21 most of methods reported, nanoparticles are functionalized with azide groups and attached to an
22 alkyne-terminated self-assembled monolayer. The opposite functionalization scheme is seldom
23 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 minutes. 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 $\text{M}\Omega\cdot\text{cm}$, 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 hours, 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 hours (based on the reaction time reported for similar systems [18]), or it was sonicated for 48 hours, as indicated in the text. In both cases, the substrate was then washed with ethanol, dichloromethane, ethanol, and sonicated in ethanol for 30 minutes.

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

1 attachment. Each spectrum was recorded as 64 scans at a resolution of 4 cm^{-1} over a range of
2 4000 cm^{-1} to 600 cm^{-1} .

3 X-ray photoelectron spectroscopy (XPS) was performed on the samples to confirm
4 covalent attachment of the nanoparticles to the surface through the “click” reaction using a
5 Thermo Scientific K-Alpha + equipped with an Al K α source ($h\nu=1486.6\text{ eV}$) at a take-off angle
6 normal to the surface. The measurements were performed in a vacuum chamber with a base
7 pressure of 5×10^{-9} mBar. Survey spectra were collected over a binding energy range of 0 eV to
8 1000 eV, with a pass energy of 100 eV, step size of 1 eV, and dwell time of 10 ms. High
9 resolution spectra were collected with a pass energy of 20 eV, step size of 0.10 eV, and dwell
10 time of 50 ms. The number of scans per cycle varied between 5 scans and 50 scans, depending
11 on the spectral region being analyzed. The Au $4f_{7/2}$ peak at 83.8 eV was used to calibrate all
12 spectra. CasaXPS software was used for data processing and peak fitting.

13 Density functional theory (DFT) calculations were performed using the Gaussian 09 Suite
14 [25] of programs with B3LYP functional [26,27] and 6-311+G(d,p) basis set. Geometry
15 optimization of the proposed intermediate species for the “click” reaction was performed. In the
16 model studies, 1-hexyne was used as the molecule providing the terminal alkyne group and
17 copper atoms were stabilized with acetonitrile ligands. The charge of Cu^{1+} was maintained by
18 placing chlorine atoms in close vicinity of the copper centers. Geometry optimization and
19 prediction of the core level XPS spectra for the N 1s were performed. The azide-terminated SAM
20 was modeled using optimized 11-azido-undecanethiol and the nanoparticle monolayer sample
21 was modeled using the optimized triazole-linked 4-pentyn-1-ol and 2-azidoethanol. The
22 computationally predicted XPS spectra were calibrated with a correction factor of 8.76 eV for
23 the 6-311+G(d,p) basis set, based on the previously published procedure [28].

3. Results and discussion

3.1. Confirmation of monolayer formation by scanning electron microscopy

The monolayers formed from both the stirring method and the sonication method were observed using scanning electron microscopy, as shown in Figure 1. Both exhibit very high surface coverage (nearly 100 %), where 100% refers to a single hexagonally close-packed layer of nanoparticles. This was determined by comparing the average center-to-center distance (20.4 ± 2.6 nm) between the nanoparticles in the monolayer (as observed with SEM) to the diameter of the nanoparticles reported by the manufacturer (18-22 nm range, with an average diameter of 20 nm). While both monolayers in Figure 1 show high surface coverage, the stirring method results in a more uniform, higher coverage nanoparticle film. The sonication method results in high coverage in most areas but also shows patches free of particles, which may indicate that the sonication of the surface removes some nanoparticles from the monolayer during the procedure or damages some of the functional groups. In both cases, the physically adsorbed nanoparticles are removed and no nanoparticles are observed beyond the monolayer formed. This shows that the sonication cleaning and rinsing steps taken to remove physically adsorbed particles and catalyst (as also confirmed by XPS studies) are sufficient, and magnetic properties of the nanoparticles do not preclude one from effective completion of this step. The coverage of the monolayer produced with this method is very high, especially when compared to those from similar systems reported in the literature [19]. The improvement in coverage is thought to be, in part, attributed to the functionalization scheme of the substrate and will be discussed in detail below. While Figure 1 assures high nanoparticle coverage, SEM cannot guarantee that the coating consists of only a single layer of nanoparticles; neither does it confirm that the

1 nanoparticles are bound via a triazole ring formed by the “click” reaction. This is especially
2 important to confirm because agglomeration is expected for magnetic materials.

3
4 **Figure 1** Scanning electron microscopy (SEM) micrographs of the magnetic monolayer on the
5 gold surface following (a) “click” reaction by a stirring method and (b) “click” reaction by a
6 sonication method.

7

8 *3.2. Interrogation of monolayer profile by atomic force microscopy*

9 Atomic force microscopy can confirm single layer formation through the analysis of
10 surface topography for monodisperse nanoparticles. Figure 2b shows the AFM micrograph of an
11 area on the fringe of the monolayer. The corresponding line profile is consistent with a formation
12 of a single layer of 20-nm nanoparticles. For comparison, Figure 2a shows the micrograph of the
13 azide-terminated gold substrate. The surface roughness observed in the corresponding line
14 profile is consistent with that at the edges of the line profile in 2b and can be attributed to the

1 evaporated gold substrate, rather than the nanoparticles. Therefore, AFM confirms that this
2 procedure forms a *single* layer of magnetic iron oxide nanoparticles instead of ordered
3 multilayers. This allows for the possibility that every nanoparticle in the monolayer is covalently
4 bound to the substrate, creating a robust film. Furthermore, the fact that only a single layer is
5 observed through AFM also suggests that the washing steps performed are sufficient to remove
6 nanoparticles that are only magnetically-bound to other particles.

7

8

Figure 2 Atomic force microscopy (AFM) micrographs and corresponding line profiles of (a) the azide-terminated gold surface and (b) an edge of the nanoparticle layer (where the average coverage is low and islands of nanoparticles can be identified) covalently-bound to the gold surface. The height of the nanoparticle layer confirms that only a single layer of 20 nm particles is formed on the surface.

3.3. Confirmation of “click” reaction by Fourier-transform infrared spectroscopy

While microscopy techniques prove that this method achieves a high-coverage monolayer of nanoparticles, they cannot provide any information on the chemical environment of the nanoparticle-substrate interface. To confirm chemical binding, attenuated total reflectance infrared spectroscopy was used to compare the azide-terminated gold substrate before and after addition of the chemically-modified iron oxide nanoparticles, as summarized in Figure 3. The presence of a peak at 2096 cm^{-1} in the spectrum of the azide-terminated surface is indicative of the azide stretch [23]. Following addition of the nanoparticles, this peak diminishes drastically, indicating that the azide group participates in a chemical reaction. The alkyne $\text{C}\equiv\text{C}$ stretch is also expected to appear in this spectral region; however, its intensity is normally very low and in previous studies it was not detected by IR for similar systems [17,29]. In addition, previous studies [17] showed that following the formation of the triazole ring, any unreacted azide can be titrated resulting in the complete disappearance of any absorption features in this spectral region, despite the presence of alkyne groups.

The peaks at 2854 cm^{-1} and 2927 cm^{-1} , representing the alkyl CH_2 stretching vibrations, indicate a slightly disordered system [30–32] on both the azide-terminated surface and the surface following modification with the nanoparticles. This is expected due to the disordered substrate of spherical nanoparticles, upon which the alkyl chains are detected on the surface following the “click” reaction, observed in spectrum (b) of Figure 3. This observation on the flat azide-terminated surface can also be explained by the fact that the ATR tip is in physical contact with the surface during the measurement, likely disrupting the order of the self-assembled monolayer. The small peak around 3270 cm^{-1} observed in spectrum (b) but not in (a) may provide further support of the presence of the alkyne-functionalized nanoparticles, as it indicates

1 the presence of the alkyne C-H stretching [29] on a background of water spectrum likely
2 corresponding to water molecules trapped within the monolayer of the nanoparticles. Spectrum
3 (b) shows strong peaks within the spectral region between 600 cm^{-1} and 1600 cm^{-1} that can be
4 attributed to several species, such as P-C, P-O, and P=O (from iron oxide nanoparticle surface
5 modification), Fe-O, and the triazole ring [18,19,30,33–38]. These features are absent in the
6 spectrum of the azide-terminated substrate. Approximate peak assignments for these species
7 based on the literature data and on computational investigations can be found in the
8 Supplementary Information.

9 The disappearance of surface azide, along with the presence of species associated with
10 the functionalized nanoparticles, including the alkyne C-H and phosphonic acid species, are
11 expected as the nanoparticles are deposited onto the substrate and the azide and alkyne groups
12 react with one another. However, the features associated with the triazole ring formation overlap
13 with other species and therefore, ATR-IR cannot provide additional quantitative information on
14 the completeness of the “click” reaction.

Figure 3 Attenuated total reflectance infrared (ATR-IR) spectra of (a) the azide-terminated gold surface, (b) the magnetic monolayer following the “click” reaction. *All spectra for (b) result from the sonication method, except for that in the rightmost panel, which resulted from the stirring method.

3.4. Confirmation of “click” reaction by X-ray photoelectron spectroscopy

In order to confirm the chemical reaction proposed, the chemical states of the surface species must be probed. X-ray photoelectron spectroscopy was used to compare the surface before and after addition of the nanoparticles. The spectrum labeled (a) in Figure 4 shows the azide-terminated gold surface in the N 1s region (top) and the Fe 2p region (bottom) and the spectrum labeled (b) represents the surface following the “click” reaction with the functionalized nanoparticles. The lack of any features in spectrum (a) corresponding to the iron 2p region is

1 expected as no iron oxide had been introduced at that point. Following addition of the
2 nanoparticles, the Fe $2p_{1/2}$ and Fe $2p_{3/2}$ features appear around 725 eV and 711 eV, respectively
3 in spectrum (b). Additionally, the presence of a satellite shake-up peak around 720 eV indicates
4 that the surface of the iron (II,III) oxide largely oxidizes to iron (III) oxide [39]. Spectrum (a) in
5 the N 1s region shows two distinct features that can be deconvoluted into three components at
6 404.4 eV, 400.9 eV, and 399.4 eV. These components can be readily assigned to the nitrogen
7 atoms of the azide group: $\text{N}=\text{N}=\text{N}-$, $\text{N}=\text{N}=\text{N}-$ and $\text{N}=\text{N}=\text{N}-$, respectively (bolded and italicized
8 for clarity) [17,38,40,41]. Density functional theory (DFT) calculations were performed to
9 predict the binding energies of nitrogen atoms in the azide group and are represented by the
10 colored lines beneath the experimental spectrum. In spectrum (b), following the “click” reaction,
11 the two distinct features from the azide nitrogens disappear and one broad peak representing the
12 triazole ring is formed. The computationally-predicted binding energies for the nitrogen atoms in
13 the triazole ring can be observed underneath the spectrum. The lower intensity for spectrum (b)
14 may be explained by attenuation of the beam by the surface-bound nanoparticles, which are not
15 present in spectrum (a). Thus, the spectra obtained by XPS confirm the addition of the magnetic
16 nanoparticles. More importantly, the spectra in the N 1s region agree with the expected results,
17 as the azide reacts to form the triazole ring and support evidence of the “click” reaction. It should
18 be mentioned that alternative reactions resulting in the azide group oxidation leading to the
19 formation of $\text{N}=\text{O}$, NO_2 , and $-\text{N}-\text{OH}$ functionalities can be ruled out because it has been shown
20 previously that all these reaction pathways would result in higher binding energy features
21 [17,42–44] not observed in the experimental spectra of the N 1s region.

Figure 4 X-ray photoelectron spectroscopy (XPS) spectra in the N 1s region (top) and the Fe 2p region (bottom). Spectrum (a) represents the azide-terminated surface and spectrum (b) represents the surface following the formation of the monolayer of iron oxide nanoparticles on the surface via the “click” reaction. Density functional theory (DFT) calculations were performed to predict the binding energies of the nitrogen atoms within the azide group and the triazole ring. The colored lines below each N 1s spectrum indicate the locations of the predicted binding energy of each nitrogen atom of corresponding color in the model.

3.5. *Explanation of effective nanoparticle deposition scheme by density functional theory calculations*

While the spectroscopy can confirm the chemistry of the covalent attachment resulting from this method, it does not explain the exceptionally high surface coverage achieved. A closer inspection of the catalysis mechanism of the “click” reaction may help explain the success of the procedure used. The originally-proposed mechanism [45] suggests that a copper (I) center is required to interact with the alkyne group to form the intermediate structure, with which the azide group can interact. More recently, new evidence [46] shows that two copper centers may be required to catalyze the reaction; one to interact with the terminal end of the group, and the other to interact with the alkyne group to form a π -complex. Density functional theory calculations were performed to compare the stabilities of the one- and two-copper center intermediates on a hexyne molecule (used to represent surface alkyne functional group), as shown in Figure 5. The energy difference of 47.9 kJ/mol, with the two-copper intermediate being the lower energy structure, suggests that the newly proposed catalytic intermediate is a very likely possibility. The two-copper intermediate structure was also shown to surround the alkyne group with considerable bulk (about 10 Å). On a flat surface with a well-ordered self-assembled monolayer of alkyne groups, the formation of the catalyst intermediate may be hindered by the closely-packed alkyl groups. The intermolecular distance between alkyl thiols on Au(111) surface is reported to be less than 5 Å for a full monolayer [47]. Therefore, even if the first copper center interacts with an alkyne moiety, the steric factors may make it nearly impossible for the second copper-containing moiety to approach. Once formed, the large intermediate may present a challenge for incoming azide groups to insert themselves into the overlayer to reach the alkyne groups and form the triazole ring. By functionalizing the spherical nanoparticles with the

alkyne monolayer instead (as is done in this work), rather than the flat substrate, the alkyne groups are less tightly-packed. This allows the copper catalyst to more easily reach the alkyne groups and the azide groups to insert into the overlayer. By allowing the azide groups better access to the alkyne, the partial disorder in the alkyne monolayer can facilitate the “click” reaction, resulting in better coverage of the nanoparticles on the substrate. For this reason, the functionalization scheme used to create these nanoparticle assemblies may prove to have a very important impact on surface coverage.

Figure 5 The scheme shows the energy difference between one- and two-copper intermediate structures determined by density functional theory (DFT) calculations and confirms the stability of the two-copper center intermediate. The structure in the red box shows that the two-copper intermediate is sterically bulky. The DFT calculations were performed using a 6-311+G(d,p) basis set and B3LYP functional.

4. Conclusions

A straightforward approach for creating a layered structure of magnetic nanoparticles using “click chemistry” was modified to increase coverage on the substrate and to ensure the

deposition of a single complete monolayer, as observed through electron microscopy techniques. The presence, or absence, of targeted functional groups in infrared spectroscopic studies, along with confirmation of the “click” reaction via XPS, attest to the covalent binding between the nanoparticles and substrate to result in a strongly-bound monolayer. Density functional theory calculations confirm spectroscopic results and provide a possible explanation to the high coverage achieved. The functionalization scheme of the nanoparticles and flat surface appears to play an important role in determining the nanoparticle coverage. This insight into the mechanism of this attachment method provides an unparalleled degree of control of the monolayer and should be considered for various applications demanding such levels of precision.

Acknowledgements

Funding of this work was provided by the National Science Foundation (CHE 1057374) and the Petroleum Research Fund, administered by the American Chemical Society. The authors would like to thank Professor T. P. Beebe, Jr., Ms. R. Pupillo, and Mr. Z. Voras (Surface Analysis Facility, University of Delaware) for XPS support, as well as the NSF (CHE 1428149) and the NIH NIGMS COBRE program (P30-GM110758) for partial support of the activities in the University of Delaware Surface Analysis Facility. They also would like to thank Professor C. Ni and Dr. F. Deng (Keck Electron Microscopy Facility, University of Delaware) and Mr. Y. Duan (Department of Chemistry, University of Delaware) for SEM and AFM support. Acknowledgement is also given to Professor K. Booksh and Dr. D. Boyne (Department of Chemistry, University of Delaware) for their support of the single point ATR instrument, as well as to Professor J. Koh and Mr. E. Zhang (Department of Chemistry, University of Delaware) for help with synthesis of the 11-azido-undecanethiol.

References

- [1] X. Luo, A. Morrin, A.J. Killard, M.R. Smyth, Application of nanoparticles in electrochemical sensors and biosensors, *Electroanalysis*. 18 (2006) 319–326.
- [2] H. Tao, L.-Z. Fan, W.-L. Song, M. Wu, X. He, X. Qu, Hollow core–shell structured Si/C nanocomposites as high-performance anode materials for lithium-ion batteries, *Nanoscale*. 6 (2014) 3138.
- [3] D. V. Talapin, J.-S. Lee, M. V. Kovalenko, E. V. Shevchenko, Prospects of Colloidal Nanocrystals for Electronic and Optoelectronic Applications, *Chem. Rev.* 110 (2010) 389–458.
- [4] S. Amigoni, E. Taffin de Givenchy, M. Dufay, F. Guittard, Covalent layer-by-layer assembled superhydrophobic organic-inorganic hybrid films, *Langmuir*. 25 (2009) 11073–11077.
- [5] A.D. Kent, Spintronics: A nanomagnet oscillator., *Nat. Mater.* 6 (2007) 399–400.
- [6] H. Ai, S. a Jones, Y.M. Lvov, Biomedical applications of electrostatic layer-by-layer nano-assembly of polymers, enzymes, and nanoparticles., *Cell Biochem. Biophys.* 39 (2003) 23–43.
- [7] C.L. Chien, Granular magnetic solids (invited), *J. Appl. Phys.* 69 (1991) 5267–5272.
- [8] I. Koh, L. Josephson, Magnetic Nanoparticle Sensors, *Sensors*. 9 (2009) 8130–8145.
- [9] S.H. Liou, Comparison of magnetic images using point and thin-film magnetic force microscopy tips, *IEEE Int. Magn. Conf.* 35 (1999) 3989–3991.
- [10] S. Takahashi, S. Maekawa, Effect of Coulomb Blockade on Magnetoresistance in

- 1 Ferromagnetic Tunnel Junctions, *Phys. Rev. Lett.* 80 (1998) 1758–1761.
- 2
- 3 [11] a. Berkowitz, J. Mitchell, M. Carey, a. Young, S. Zhang, F. Spada, et al., Giant
4 magnetoresistance in heterogeneous Cu-Co alloys, *Phys. Rev. Lett.* 68 (1992) 3745–3748.
5
- 6 [12] G.N. Parsons, J.W. Elam, S.M. George, S. Haukka, H. Jeon, W.M.M. (Erwin) Kessels, et
7 al., History of atomic layer deposition and its relationship with the American Vacuum
8 Society, *J. Vac. Sci. Technol. A Vacuum, Surfaces, Film.* 31 (2013) 050818.
9
- 10 [13] J. Borges, J.F. Mano, Molecular Interactions Driving the Layer-by-Layer Assembly of
11 Multilayers., *Chem. Rev.* 114 (2014) 8883–8942.
12
- 13 [14] Y. Gao, J. Qi, J.J. Zhang, S. Kang, W. Qiao, M. Li, et al., Fabrication of both the
14 photoactive layer and the electrode by electrochemical assembly: towards a fully solution-
15 processable device., *Chem. Commun. (Camb).* 50 (2014) 10448–51.
16
- 17 [15] S.T. Dubas, P. Kumlangdudsana, P. Potiyaraj, Layer-by-layer deposition of antimicrobial
18 silver nanoparticles on textile fibers, *Colloids Surfaces A Physicochem. Eng. Asp.* 289
19 (2006) 105–109.
20
- 21 [16] J. Kao, K. Thorkelsson, P. Bai, Z. Zhang, C. Sun, T. Xu, Rapid fabrication of
22 hierarchically structured supramolecular nanocomposite thin films in one minute., *Nat.*
23 *Commun.* 5 (2014) 4053.
24
- 25 [17] Y. Liu, M.G. Williams, T.J. Miller, A. V. Teplyakov, Nanoparticle Layer Deposition
26 (NPLD) for highly controlled multilayer formation based on high-coverage monolayers of
27 nanoparticles, (submitted to *Langmuir*). (n.d.).
28
- 29 [18] D. Toulemon, B.P. Pichon, X. Cattoën, M.W.C. Man, S. Begin-Colin, 2D assembly of
30 non-interacting magnetic iron oxide nanoparticles via “click” chemistry, *Chem. Commun.*
31 47 (2011) 11954–11956.
32
- 33 [19] D. Toulemon, B.P. Pichon, C. Leuvrey, S. Zafeiratos, V. Papaefthimiou, X. Cattoën, et al.,
34 Fast assembling of magnetic iron oxide nanoparticles by microwave-assisted copper(I)
35 catalyzed alkyne-azide cycloaddition (CuAAC), *Chem. Mater.* 25 (2013) 2849–2854.
36
- 37 [20] A.P. Upadhyay, D.K. Behara, G.P. Sharma, A. Bajpai, N. Sharac, R. Ragan, et al.,
38 Generic process for highly stable metallic nanoparticle-semiconductor heterostructures via
39 click chemistry for electro/photocatalytic applications, *ACS Appl. Mater. Interfaces.* 5

- (2013) 9554–9562.
- [21] S. Kinge, T. Gang, W.J.M. Naber, W.G. Van Der Wiel, D.N. Reinhoudt, Magnetic nanoparticle assembly on surfaces using click chemistry, *Langmuir*. 27 (2011) 570–574.
- [22] H.C. Kolb, M.G. Finn, K.B. Sharpless, Click Chemistry: Diverse Chemical Function from a Few Good Reactions, *Angew. Chemie - Int. Ed.* 40 (2001) 2004–2021.
- [23] J.P. Collman, N.K. Devaraj, C.E.D. Chidsey, “Clicking” Functionality onto Electrode Surfaces, *Langmuir*. 20 (2004) 1051–1053.
- [24] D. Nečas, P. Klapetek, Gwyddion: an open-source software for SPM data analysis, *Cent. Eur. J. Phys.* 10 (2012) 181–188.
- [25] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, et al., *Gaussian 09*, Revision B.01, (2009).
- [26] C. Lee, W. Yang, R.G. Parr, Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density, *Phys. Rev. B.* 37 (1988) 785–789.
- [27] A.D. Becke, A new mixing of Hartree–Fock and local density-functional theories, *J. Chem. Phys.* 98 (1993) 1372.
- [28] T.R. Leftwich, A. V. Teplyakov, Calibration of computationally predicted N 1s binding energies by comparison with X-ray photoelectron spectroscopy measurements, *J. Electron Spectros. Relat. Phenomena.* 175 (2009) 31–40.
- [29] P. Paoprasert, J.W. Spalenska, D.L. Peterson, R.E. Ruther, R.J. Hamers, P.G. Evans, et al., Grafting of poly(3-hexylthiophene) brushes on oxides using click chemistry, *J. Mater. Chem.* 20 (2010) 2651.
- [30] A.B. Sieval, R. Linke, G. Heij, G. Meijer, H. Zuilhof, E.J.R. Sudhölter, Amino-terminated organic monolayers on hydrogen-terminated silicon surfaces, *Langmuir*. 17 (2001) 7554–7559.
- [31] M. Perring, S. Dutta, S. Arafat, M. Mitchell, P.J. a Kenis, N.B. Bowden, Simple Methods for the Direct Assembly , Functionalization , and Patterning of Acid-Terminated Monolayers on Si (111) Simple Methods for the Direct Assembly , Functionalization , and Patterning of Acid-Terminated Monolayers on Si (111), *Tempo.* (2005) 10537–

- 10544.
- [32] F. Tian, C. Ni, A. V. Teplyakov, Integrity of functional self-assembled monolayers on hydrogen-terminated silicon-on-insulator wafers, *Appl. Surf. Sci.* 257 (2010) 1314–1318.
- [33] R. Artzi Daube, S.S., Cohen, H., Naaman, R., Adsorption of organic phosphate as a means to bind biological molecules to GaAs surfaces, *Langmuir*. 19 (2003) 7392–7398.
- [34] T.J. Daou, J.M. Grenche, F. Thomas, A. Derory, P. Bernhardt, P. Legar, et al., Phosphate Adsorption Properties of Magnetite-Based Nanoparticles Phosphate Adsorption Properties of Magnetite-Based Nanoparticles, *Chem. Mater.* 19 (2007) 4494–4505.
- [35] R.C. Longo, K. Cho, W.G. Schmidt, Y.J. Chabal, P. Thissen, Monolayer doping via phosphonic acid grafting on silicon: Microscopic insight from infrared spectroscopy and density functional theory calculations, *Adv. Funct. Mater.* 23 (2013) 3471–3477.
- [36] M. a White, J. a Johnson, J.T. Koberstein, N.J. Turro, Toward the Syntheses of Universal Ligands for Metal Oxide Surfaces : Controlling Surface Functionality through Click Chemistry Toward the Syntheses of Universal Ligands for Metal Oxide Surfaces : Controlling Surface Functionality through Click Chemistry, *J. Am. Chem. Soc.* 128 (2006) 11356–11357.
- [37] F. Billes, H. Endrédi, G. Keresztury, Vibrational spectroscopy of triazoles and tetrazole, *J. Mol. Struct. THEOCHEM.* 530 (2000) 183–200.
- [38] Y. Liu, N. RamaRao, T. Miller, G. Hadjipanayis, A. V. Teplyakov, Controlling Physical Properties of Iron Nanoparticles during Assembly by “Click Chemistry,” *J. Phys. Chem. C.* 117 (2013) 19974–19983.
- [39] M. Muhler, R. Schlögl, G. Ertl, The nature of the iron oxide-based catalyst for dehydrogenation of ethylbenzene to styrene 2. Surface chemistry of the active phase, *J. Catal.* 138 (1992) 413–444.
- [40] A. Devadoss, C.E.D. Chidsey, Azide-modified graphitic surfaces for covalent attachment of alkyne-terminated molecules by “click” chemistry, *J. Am. Chem. Soc.* 129 (2007) 5370–5371.
- [41] a. C. Gouget-Laemmel, J. Yang, M. a. Lodhi, a. Siriwardena, D. Aureau, R. Boukherroub, et al., Functionalization of azide-terminated silicon surfaces with glycans

- 1 using click chemistry: XPS and FTIR study, J. Phys. Chem. C. 117 (2013) 368–375.
2
- 3 [42] F. Tian, D.F. Taber, A. V. Teplyakov, NH- termination of the Si(111) surface by wet
4 chemistry, J. Am. Chem. Soc. 133 (2011) 20769–20777.
5
- 6 [43] T. Miller, A. V. Teplyakov, Attachment chemistry of PCBM to a primary-amine-
7 terminated organic monolayer on a si(111) surface, Langmuir. 30 (2014) 5105–5114.
8
- 9 [44] F. Gao, A. V Teplyakov, Reaction of Hydrazine with a Chlorine-Terminated Si (111)
10 Surface, J. Phys. Chem. C. 118 (2014) 27998–28006.
11
- 12 [45] F. Himo, T. Lovell, R. Hilgraf, V. V. Rostovtsev, L. Noodleman, K.B. Sharpless, et al.,
13 Copper(I)-catalyzed synthesis of azoles. DFT study predicts unprecedented reactivity and
14 intermediates, J. Am. Chem. Soc. 127 (2005) 210–216.
15
- 16 [46] B.T. Worrell, J.A. Malik, V. V Fokin, Direct evidence of a dinuclear copper intermediate
17 in Cu(I)-catalyzed azide-alkyne cycloadditions., Science. 340 (2013) 457–60.
18
- 19 [47] C. Vericat, M.E. Vela, R.C. Salvarezza, Self-assembled monolayers of alkanethiols on
20 Au(111): surface structures, defects and dynamics., Phys. Chem. Chem. Phys. 7 (2005)
21 3258–3268.

1

Graphical Abstract

2