A perspective on the magnetism of alkanethiol-coated gold thin films

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A perspective on the magnetism of alkanethiol-coated gold thin films

Pengcheng Dong and Simon Trudel

Abstract: Intriguing ferromagnetic behaviour has been reported in gold thin films – a diamagnetic material in the bulk – wherein large magnetic moments and uncommon anisotropy are often hallmark features. The tuning of the electronic and magnetic properties by the presence of molecular self-assembled monolayers has been proposed. In this work, we present the study of the magnetism of a wide collection of alkanethiols of differing chain lengths coated on Au. We find no or only very weak magnetism, casting doubt on the universality and reproducibility of this phenomenon.

Key words: magnetic thin films, gold nanostructures, unconventional magnetism, self-assembled monolayers.

Résumé: Un comportement ferromagnétique intrigant a été rapporté pour des couches minces d’or - un matériau diamagnétique dans le vrac - où de larges moments magnétiques et une anisotropie peu commune sont souvent présents. La modification des propriétés électroniques et magnétiques par la présence de monocouches moléculaires auto-assemblées a été proposé. Dans ce travail, nous présentons l’étude du magnétisme d’une large collection d’alcanethiols de différentes longueurs de chaînes auto-assemblés sur une surface d’or. Nous ne trouvons aucun ou seulement un très faible magnétisme, jetant le doute sur l’universalité et la reproductibilité de ce phénomène.

Mots clés : couches minces magnétiques, nanostructures à base d’or, magnétisme non-conventionnel, monochouches auto-assemblées.

1. Introduction

Ferromagnetism is usually only possible in materials in which the constituent atoms have partially-filled d or f orbitals. However, only a few of the 3d, 4d and 5d transition metals that have unfilled d orbitals form magnetic solids, and none of the 4d or 5d elements is ferromagnetic in the bulk.1 In the bulk, the only ferromagnetic elements are iron, cobalt and nickel. Most magnetic compounds incorporate these magnetic elements, except for a few alloys made from otherwise non-magnetic elements.2–4

Metals such as Au, Ag and Cu have filled outer d orbitals, are diamagnetic in bulk form, and the first two are among the noble metals due to their inert chemical behaviour. Thus, the discovery of magnetic nanostructures made from these metals was surprising.5–11 In the case of gold, magnetism has been found for both nanoparticles12–19 and thin films.20–25 Indeed, nanostructuring is known to lead to many unexpected discoveries. Nanoparticles (NPs), due to their small size and pronounced surface effects, often display significantly different properties from their bulk counterparts.

In 1999, Hori et al. opened up the realm of gold magnetism with their finding of polymer-coated Au NPs that showed unexpected large magnetic moments of \( \approx 20 \mu_B \) per particle.26 From that moment on, the presence of magnetism in gold nanoparticles has been widely reported.5,6 In most cases, the nanoparticles were coated with organic ligands, the majority including a thiol functional group for attachment to the gold surface. Agreement is harder to find in essentially all other aspects. The magnetization vs field, \( M(H) \), reversal curves displayed either paramagnetism or soft ferromagnetism.12,15,19,27 The magnetization was seen to reach saturation,11,16 with the \( M_s \) being small28 or rather large.11 The highest reported saturation moment is 5 emu g \(^{-1}\) (or \( \approx 35 \mu_B \) per particle, or 0.33 \( \mu_B \) per magnetic atom), found in Au NPs coated with poly(aniline).29 The coercive field \( H_c \) could reach as high as 86 mT.29 Yet in some reports the magnetization did not saturate at all.18,21 It seems every experimentally observed trend has an equal and opposite rebuttal.

There are much fewer reports on the magnetism of gold films.20–25 Several reports found strong anisotropic magnetization in gold thin films coated by self-assembled monolayers (SAMs), wherein the magnetization was preferentially in the out-of-plane direction and appears to be paramagnetic or weakly ferromagnetic.20,21,24 The study of azobenzene-coated Au thin films provided strong evidence that the capping molecule – and in particular its dipole moment – strongly affects the observed magnetism.24 Interestingly, in another work uncoated gold thin-films deposited on glass were found to become paramagnetic when temperature was lowered to 5 K.23

To further probe the effect of the SAM, we measured a series of polycrystalline gold substrates onto which alkanethiols of varying chain lengths were electrodeposited. Alkanethiols are known for showing odd-even effects, wherein the orientation of the terminal methyl group changes the dipole moment of the molecule, therefore affecting several properties such as wettability, reactivity, phase transitions, and work function.29,30 We initially set out to see if such odd-even effects would be present in the magnetism of self-assembled monolayers of alkanethiols adsorbed on Au substrates. What we instead found – or
more precisely didn’t find – are an absence of strong magnetic moments, anisotropy, and chain-length dependence. As is reminiscent of the better-documented Au NPs, the moments are spread over a range spanning almost 4 orders of magnitude, with the films presented here setting the lower bar compared to those previously reported, casting doubt into our understanding of these systems.

2. Experimental

2.1. Chemicals

Gold thin-film substrates were 100 nm-thick films of sputtered polycrystalline gold (99.999%) on a [100]-oriented silicon wafer, with a 5 nm-thick titanium (99.99%) adhesive layer, purchased from Sigma-Aldrich. For electrochemical work, water was purified through a Barnstead E-Pure reverse-osmosis system which purifies water to reach a resistivity of 18.2 MΩ·cm⁻¹. 1-pentanethiol (98.5%), 1-hexanethiol (98.5%), 1-heptanethiol (99%), 1-dodecanethiol (98%), 1-octadecanethiol (99.5%) and anhydrous ethanol were obtained from Sigma-Aldrich. 1-butanol (98%), 1-octanol (98%), 1-nonanol (99.5%), 1-decanol (98%), 1-undecanethiol (98%) were obtained from Alfa Aesar. 1-tetradecanethiol (99%) was obtained from Fisher. Concentrated sulfuric acid was purchased from EMDC Chemicals. Concentrated hydrogen peroxide was obtained from Merck. Magnesium sulfate (99%) and potassium perchlorate dihydrate (99.5%) were obtained from Baker Analytical. VGE-7031 adhesive was used for attachment of samples for measurement using the SQUID magnetometer.

Ethanol was distilled to further purify it. First, the perchlorate electrolyte (a hydrate) was added to ethanol, and the ethanolic solution distilled, followed by drying through mixing with anhydrous magnesium sulfate, which was subsequently filtered out.

2.2. Cleaning of gold

To remove organic surface contaminants prior to SAM deposition, gold films were cleaned by immersing them in Piranha (1:4 H₂O₂(30%):H₂SO₄(18 M)) for 1 minute at room temperature, and rinsed with copious amounts of water. The film would then be washed with methanol followed by acetone before being subjected to 20 volatilization cycles in dilute 0.05 M aqueous H₂SO₄, ending with the reductive voltage, to return any oxidized gold to its metallic state, and also standardize the surface before use. This gold would be used immediately. WARNING: While we encountered no difficulty using Piranha solutions, care must be taken to prevent uncontrolled violent reactions with organic substances.

2.3. Thiol attachment

Alkanethiols with various number of carbons atoms (n = 4, 5, 6, 7, 8, 9, 10, 11, 12, 14, 18) were electrodeposited. These alkanethiols and the gold films coated by them will be referred to as n-H.

For all electrochemical work a Princeton Applied Research Versastat-3 potentiostat was used. The reference electrode for experiments in both aqueous and ethanolic solutions was a Hg/HgSO₄ electrode with a frit diaphragm (London Scientific). The electrochemical cell consisted of a three-neck round-bottomed flask, fitted with alligator clips to which electrodes including the counter electrode (Pt sheet, Strem Chemicals), were attached.

Modifying a procedure from Brett et al., the deposition was carried out in 1 mM ethanoic solution of oxalic acid, with 0.1 M potassium perchlorate as supporting electrolyte. The solution was purged with nitrogen for 30 minutes, and remained under a nitrogen environment during the deposition. The thiol was added with an Eppendorf pipette. The electrochemical step began with an initial desorption process at -1.9 V for 1 minute, followed by electrodeposition at 0.19 V for 5 minutes (all potentials here are vs the Hg/HgSO₄ reference electrode). The coated film was washed with distilled ethanol, dried under a stream of nitrogen, and stored in air.

2.4. XPS

X-ray photoelectron spectroscopy (XPS) was performed using a Kratos Analytical XPS spectrometer (Alberta Center for Surface Engineering and Science, University of Alberta) for Au films coated by dodecanethiol. XPS spectra were analyzed using the CasaXPS software. The energy shift were corrected using the adventitious surface carbon peak at 284.8 eV. Baselines were fitted with the Shirley function, and the peaks fit with a GL(30) profile.

2.5. SQUID magnetometry

All magnetic measurements were carried out in a Quantum Design XL-7S superconducting quantum interference device (SQUID) magnetometer. Magnetization was measured for two directions of applied field: along (magnetization-in-plane, MIP) and perpendicular (magnetization perpendicular-to-the-plane, MPP) to the film-plane. For MIP measurements, a 4 mm × 4 mm film sample was stuck in a clear and diamagnetic plastic straw, so that the plane lies parallel to the straw’s long axis. For MPP measurements, a slightly smaller film sample was stuck in the straw similarly. Magnetization reversal loops were measured at temperatures of 300 K and 1.9 K.

Since the absolute moment of the film samples is small, over the entire range of the applied field the magnetic response is dominated by diamagnetism; as a result the response appears nearly linear, with a negative slope. A straw holder containing an unprocessed gold film was made for magnetic measurement alone, and its contribution subtracted out. All presented results are diamagnetism-corrected, and normalized to the geometric surface area of the substrate.

3. Results and Discussion

3.1. XPS

A binding energy of 84.3 eV for the Au 4f7/2 peak for an unprocessed gold film is a little higher than expected (84.0 eV, Figure 1). The same peak would be shifted to a much higher 86.5 eV for Au(III). The observed binding energy (and the absence of additional Au 4f peaks) is deemed to be consistent with metallic Au. After deposition of dodecanethiol, the Au 4f7/2 peak is at 83.8 eV, which is within the range (83.8 -
Fig. 1. High-resolution XPS showing (a.) Shirley baseline-corrected Au 4f peaks for uncoated and dodecanethiol-coated gold films, and (b.) the S 2p peaks for the coated sample.

84.0 eV) found by Lennox et al. for Au films covered by thiol SAMs.\(^3\)

The S 2p\(_{3/2}\) peak is routinely used to characterize thiol bonding to gold, and the value we found (161.5 eV) is slightly lower than the often-cited value of 162.0 eV. This slight shift however does not indicate a bad-quality SAM, in which case a shift to higher energy would be expected.\(^3\) Peaks in the 163–164 eV range are indicative of unbound thiol, or thiols in multilayers; this is not seen in our sample. Finally, the absence of other peaks further precludes the presence of unattached thiols.\(^3,33\)

3.2. Magnetometry

We start with a cautionary example illustrating the challenges we encountered in studying the magnetism of these samples. Figure 2 shows an \(M(H)\) curve for a 18-H sample at 1.9 K, apparently showing a noisy hysteresis loop, with relatively high coercivity and clear remanence. The reliability of each individual data point in a SQUID measurement can be independently assessed by looking at the quality of the fit between the raw data – i.e., the SQUID voltage vs sample position as it is passed through the pick-up coils – and the equation used to fit it, from which the moment is extracted (a longitudinal regression fit value of 0.9 is a typical minimum threshold value for data considered reliable). Upon examining the regression values in this particular measurement, it is found that the majority of the data is not reliable, rendering such a measurement a false positive. This illustrates that great care must be taken while interpreting such data. More importantly, it indicates the sample’s magnetic moment is very low. Henceforth, all data presented have acceptable regression values, and while the data may be noisy as a consequence of the low moments encountered, the data is judged to be reliable.

Figure 3a compiles \(M(H)\) results that are considered reliable. These results present the expected behaviour for weakly ferromagnetic samples: sharp rise in magnetism, presence of hysteresis, and saturation. Despite noisy data, these samples may be considered as preventative of very weakly magnetic materials. On the other hand, in Figure 3b the magnetization is so low that the behaviour can be difficult to quantify or even qualitatively categorize. For example, 14-H seems to be ferromagnetic, but the noise level is comparable to its remanence. 8-H appears almost non-magnetic. As for 7-H and 11-H, the shape of their hysteresis loops is starting to look nonsensical; therefore these results probably represent only measurement errors and/or artefacts. We have to consider such samples as non-magnetic, as we have no good evidence of their magnetism. The absolute moment seen for such measurements is often below \(10^{-8}\) emu, which is near the detection limit of our instrument.

We will henceforth only interpret the first category of measurements (results such as found in Figure 3a).

\(M(H)\) measured in the MPP configuration for a variety of coated films are shown in Figure 4a-b for \(T = 300\) K and 1.9 K, respectively. Figure 4c-d presents data for the MIP configuration, also at 300 K and 1.9 K, respectively. Even though the entire series from 4-H to 18-H were studied, not all measurements made the reliability criterion, and were thus discarded, despite thorough measurement optimization and multiple independent trials. In general it can be seen the saturation magneti-
zation is reached in a field of around 0.2 to 0.5 T, and is on the order of a few $10^{-6}$ emu per cm$^2$ of gold, which is very low.

Comparing measurements made at 300 and 1.9 K, it is apparent there is very little temperature-dependence. In fact, in some cases the magnetization at 300 K may be slightly higher, if we take 18-H as an example. The effect of increased temperature generally induces thermal fluctuation which makes magnetization reversal more likely. However, the weak temperature dependence of magnetism in Au nanostructures has been reported multiple times.\(^5,6\)

The direction of anisotropy is unexpected: several studies indicate the perpendicular (MPP) direction to be favoured.\(^20,21,24\) We see the opposite; for both 14-H and 18-H in particular, the magnetization prefers to stay in-plane. In addition, the anisotropy displayed by the $M_s$ is also low: this is unexpected too, because the planar surface is highly anisotropic, so is the electronic environment imposed by the charge redistribution from gold to sulfur.

The next obvious consideration is the trend associated with chain-length of the alkanethiols, with differing molecular dipoles. The underlying hypothesis here considers the relation between the work function and molecular dipole induced by the SAM which is perpendicular to the metal surface ($\mu_\perp$), namely

$$\Delta \Phi = \frac{-N \mu_\perp}{\kappa \epsilon_0}$$

where $N$ is the density of molecules on the surface, $\epsilon_0$ is the permittivity of free space, $\kappa$ is the dielectric constant of the SAM, and $\Delta \Phi$ is the change in the work function of gold in the presence of a SAM. Einaga et al. have used this relationship to explain the modulation of the magnetism in azobenzene-modified Au NPs\(^12,40^\) and thin films.\(^24\) In the case of azobenzene, the molecular dipole depends on the cis-trans isomerization, and takes the value of -0.52 D for the trans isomer and 1.77 D for the cis isomer (here a positive dipole moment points out of surface). The cis isomer is more analogous to our case, with 1.37 D for 18-H. But Einaga’s trans isomer (-0.52 D) results in the more magnetic sample. According to Einaga et al., once the work function is increased (from the cis-trans photoisomerization), the charge transfer from gold towards the organic layer is increased, leading to more holes in gold’s $d$ band,\(^24\) which presumably modifies the magnetism.

From Figures 4 and 5 there is no trend to be seen as a function of chain length; the chain length does not play a decisive role in modulating the magnetization in these samples. This may be because the change in molecular dipole between the alkanethiols used is too small; alternatively, maybe other effects (e.g., differing packing densities, or substrate surface roughness) mask these effects. According to this analysis, a set of thiols with more electronegative terminal groups should induce a stronger magnetization, than a series of alkanethiols. In this case, if the moments may be higher, the confirmation or refutation of this prediction may be facilitated.
Table 1. Comparison of reported saturated magnetization

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<th>Sample</th>
<th>(M_s) ((\mu)emu cm(^{-2}))</th>
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<tr>
<td>C4-C18 alkanethiols</td>
<td>0.7 to 7</td>
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<tr>
<td>poly(alanine)</td>
<td>13 to 190</td>
</tr>
<tr>
<td>ethane thiol</td>
<td>26.7 to 33.0</td>
</tr>
<tr>
<td>Bi/Au bilayers</td>
<td>23 to 33</td>
</tr>
<tr>
<td>Au on Pyrex</td>
<td>73.3</td>
</tr>
<tr>
<td>octadecanethiol</td>
<td>760</td>
</tr>
<tr>
<td>azobenzene derivative</td>
<td>2000</td>
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\(a\) this work; \(b\) SAM-free samples

3.3. Comparison with previous reports

We compare the magnetization values we observed to previously published reports for SAM-coated Au thin films in Figure 5 and Table 1. These include Au thins films with SAMs of a Lewis conjugate,\(^a\) azobenzene derivative,\(^b\) poly(alanine),\(^a\) octadecanethiol, poly(alanine),\(^b\) ethane thiol,\(^a\) as well as SAM-free Au on Pyrex\(^a\) and Bi/Au bilayers.\(^b\) The first thing to be noticed is that a very wide range of saturation magnetization values have been reported, from below 10\(^{-6}\) emu cm\(^{-2}\) to over 2 \(\times\) 10\(^{3}\) emu cm\(^{-2}\), spanning close to 4 orders of magnitude. This is not unlike the compilation of saturation magnetization reported for NPs,\(^c\) which shows an equally baffling spread. We also make note that our films set the lower bar, as is indicated by the noisy measurements. While the majority of the presented samples are not alkanethiols, we can directly compare our results to those of Carmeli et al. that measured saturation values of ca. 30 and 73 \(\mu\)emu cm\(^{-2}\),\(^d\) a full order of magnitude above our own results.

The low moments and low signal-to-noise indicate our thin films are not very significantly different from the uncoated substrates. We do not believe we have missed the magnetism – we have studied enough samples to be confident the magnetism is near-absent in these films, unlike previous reports. This leaves two possible explanations. First, maybe there are factors that are not yet recognized and proven to be more critical than the mere presence of a thiol to induce magnetism, which may include surface roughness, packing density of the SAM, disorder of the molecules in the SAM, or preparation method. Second, it may be that previous reports have inadvertently reported on impurities, or measurements artefacts (we ourselves encountered such a possibility, c.f. Figure 2 and related discussion).\(^e\)\(^f\) Examples abound of reports on seemingly magnetic materials wherein a spurious, hard-to-detect species is present.\(^g\)\(^h\) In the field of unconventional magnetism in coinage metals, we recently reported that the magnetism in Ag and Cu thin films and nanoparticles arose from non-stoichiometric oxidation of the sample’s surface.\(^i\)\(^j\) While Au is less prone to oxidation (and not observed in the XPS spectra), such interfacial effects are hard to rule out.

Surface-sensitive, element specific probes (such as \(^{197}\)Au Mössbauer conversion electron spectroscopy or x-ray magnetic circular dichroism) may shed more light on this issue. An another unknown is the domain structure of these magnetic materials. It is yet unknown whether the magnetism is uniform in these thin films, or maybe localized in specific regions.

What are the implications for Au NP magnetism? To start with, NP measurements are easier for the simple reason that the samples are larger. This in itself lends more credence to the measurements. For a thin film, the sample size is limited to a few mm\(^2\), of which only a monolayer is expected to contribute to magnetism, leading to inherently low absolute moments. However, as for the Au NP magnetism,\(^c\) there appears to be a large scatter of data – pointing to a clear lack of understanding in the factors determining the magnitude in these unconventional nanomagnets. It may be that further reports will indicate two regimes: one governed by inherent magnetism of the Au nanostructures, and another where extrinsic sources of magnetism are at play.

4. Conclusions

We have attempted to study the magnetism in alkanethiol SAM-coated Au thin films. The measurements indicate very low – if any – magnetism in these samples. We also caution that seemingly magnetic samples may actually be due to measurement artefacts. These result cast some doubt on other reports of magnetism in Au thins, or at least brings into question the simplicity, universality, and reproducibility of this phenomenon. The wide spread of magnetization values reported — spanning near 4 orders of magnitude — clearly demonstrate a complete understanding of the factors affecting this unconventional magnetism is still sorely lacking.

5. Acknowledgments

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