Measuring the Size Dependence of the Magnetic Properties of Alkanethiol-Coated Gold Nanocrystals

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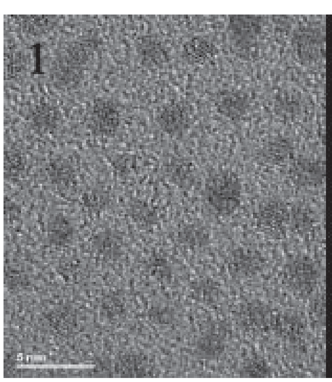
Abstract:

Bulk gold (Au) is diamagnetic but 2 nm dodecanethiol (thiol) capped gold nanoparticles (NPs) have been reported to exhibit ferromagnetism. This ferromagnetism is believed to result from spin-orbit coupling between surface-bound thiols and gold surface atoms. As the gold nanoparticle size decreases and the surface area to volume ratio increases, the likelihood of ferromagnetism increases.

The size dependence of the magnetic properties of thiol-capped gold nanocrystals was studied. Thiol-capped gold nanocrystals ranging from 2 to 6 nm in diameter were synthesized using colloidal methods. Their magnetic susceptibilities were measured using a superconducting quantum interference device (SQUID) at room temperature and 5 Kelvin (K). Contrary to two published reports, but consistent with another study, the thiol-coated gold nanocrystals did not exhibit ferromagnetism, even with diameters of 1.8 nm.

Introduction:

The high surface area-to-volume ratio in nanocrystals can lead to unexpected properties. Of interest here is the past observation that Au can become paramagnetic—and even ferromagnetic under some conditions-when the diameter is small enough—even though it is diamagnetic as a bulk material. Diamagnetic susceptibilities are small and negative, whereas paramagnetic materials have small positive susceptibilities. Ferromagnets have large positive susceptibilities and below their Curie temperature spontaneously magnetize. The objective of this research project was to determine the size dependence of the magnetic susceptibility of Au NPs and how capping ligand chemistry influences their magnetic properties. Thiol-capped Au NPs were synthesized with 2 nm and 6 nm average diameters. Au NPs were also synthesized with tetraoctylammonium bromide (TOAB), polyvinyl pyrolidone (PVP), and polyally amine hydrocloride (PAAHC) as capping ligands. The magnetic properties of the nanocrystals were measured at 5K and room temperature.



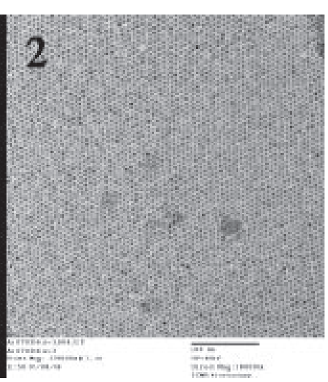


Figure 1: Hi-Res TEM image of 1.8 ± 0.26 nm Au Nps.

Figure 2: Low-Res TEM image of 5.5 ± 0.62 nm Au Nps.

Experimental Procedure:

2 nm thiol-capped gold NPs were prepared by arrested precipitation [2,7]. An aqueous solution (15 mL, 0.03M) of hydrogen tetrachloroaurate-hydrate, and an organic solution of TOAB (40 mL, 0.12M) in toluene were prepared, combined, and stirred vigorously for 30 minutes. TOAB complexes with the gold salt and transfers it to the organic solution. After 30 minutes of stirring the two phases were separated and the organic phase was retained. Dodecanethiol (0.4028 mL) was added to the organic solution. A freshly prepared aqueous reducing solution of sodium borohydride (12.5 mL, 0.40M) was mixed with the organic solution and stirred vigorously for 2 hours. The NPs were isolated by precipitation with methanol followed by centrifugation at 10°C and 8000 rpm for 10 minutes. By TEM, the NPs had a diameter of 1.8 ± 0.26 nm.

Larger diameter (6 nm) Au NPs were synthesized by reducing the TOAB:Au salt complex prior to adding dodecanethiol. TOAB serves as the capping ligand, but its weaker bonding with the Au surface enables larger particles to be obtained. 24 hrs after adding the sodium borohydride reducing solution (30 mL, 0.40 M), 240 μL of dodecanethiol was added. These NPS were precipitated with methanol and isolated by centrifugation. According to TEM, the Au NPs had an average diameter of 5.5 ± 0.62 nm.

SQUID Sample Preparation:

Kapton® tape was placed adhesive side up and Au NPs were drop-cast onto the tape and dried. The Kapton® tape with the sample was then wrapped around a quartz tube, sandwiching the sample between the two. The quartz tube was inserted into a straw to measure the magnetic response of the Au NPs.

Quartz Sample Blank:

To ensure accurate magnetic measurements, the background—including the quartz tube and Kapton® tape—was measured and subtracted. The scanned length of the quartz tubing was ~ 4 cm with a weight of ~ 0.64g. The magnetic susceptibility of of bulk quartz is $\chi_{tabulated} = -1.03 \times 10^{-9}$ emu/gOe. Copper(II) oxide (CuO) was used as a standard to check that the sample was properly cantered and that the instrument was accurately calibrated. The magnetic susceptibility of CuO is $\chi_{bulk} = 2.99 \times 10^{-6}$ emu/gOe. Measurements of CuO showed a paramagnetic response comparable to the literature value.

Results and Conclusions:

Both 1.8 nm and 5.5 nm diameter thiol capped Au NPs exhibited diamagnetic responses at 5K and 300K with magnetic susceptibilities of $\chi_{5K} = -1 \times 10^{-7}$ *emu/gOe*, $\chi_{300K} = -9 \times 10^{-7}$ *emu/gOe*, $\chi_{5K} = -3 \times 10^{-7}$ *emu/gOe* and $\chi_{300K} = -6 \times 10^{-7}$ *emu/gOe*, which is in good agreement with bulk Au, $\chi_{bulk} = -1 \times 10^{-7}$ *emu/gOe*. To ensure that there was a measurable signal from the sample above the background, 13.8 mg of the 1.8 nm diameter NPs and 9.62 mg of the 5.5 nm diameter NPs were measured. These data appear to indicate that dodecanthiolcapped Au NPs are diamagnetic, regardless of size. Further research, however, is needed to confirm whether this is indeed the case. PVP-capped Au NPs were also synthesized, but their magnetic response has not yet been measured.

In conclusion, Au NPs were synthesized using colloidal methods and their magnetic properties were measured at 5K and 300K using SQUID magnetometry. The thiol-coated Au nanocrystals appear to be diamagnetic down to diameters of 1.8 nm. No evidence of ferromagnetism at temperatures 5K and higher was observed in any samples.

Future Work:

Future work includes exploring variations of Au NP capping ligand chemistry. PVP has been reported to give rise to larger paramagnetic signals than the thiols, for example. Transition metals, like Pt, are particularly interesting for future studies and a comparison to Au.

Acknowledgements:

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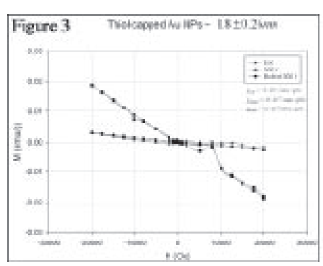

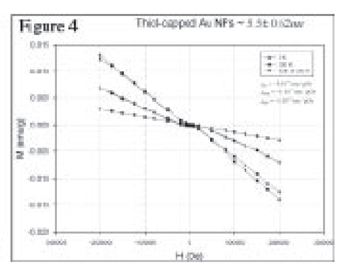

Figure 3: SQUID data ~ 1.8 ± 0.26 nm Au NPs on quartz tubing.

Figure 4: SQUID data ~ 5.5 ± 0.62 nm Au NPs on quartz tubing.