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Electronic Supplementary Information: On the origin of the ferromagnetic signature in Ag nanoparticles and thin films

Armando J. Marenco,^a David B. Pedersen,^{*b} and Simon Trudel^{*a}

^a Department of Chemistry and Institute for Quantum Science and Technology, University of Calgary, 2500 University Drive NW, Calgary, AB, Canada, T2N 1N4; ^b Centre for Security Science, Defence Research and Development Canada, 222 Nepean Street, 11th Floor, Ottawa, ON, Canada K1A 0K2 E-mail: david.pedersen@drdc-rddc.gc.ca, trudels@ucalgary.ca

Table

Table S1 displays the parameters utilized during the preparation of Ag NPs.

NP diameter	Ar flow rate	He flow rate	Ι	V	D	р
(nm)	(sccm)	(sccm)	(mA)	(V)	(cm)	(Pa)
3.3 ± 0.9	50.5	80.7	253	266.3	6	61.3
5.0 ± 0.9	50.1	50.7	253	259.8	9	50.6
7.7 ± 1.3	90.2	0	235	263.1	9	45.3

Table S1 Conditions for the generation of Ag NPs of different diameters. I is the sputtering current, V is the sputtering voltage, D is the distance of the metal target to the aggregation chamber exit, p is the pressure in the aggregation chamber during deposition.

Figures

Figure S1 shows the experimental *in situ* mass spectrometry for two Ag NP diameters 5.0 \pm 0.9 and 7.8 \pm 1.3 nm fitted with two Gaussian peaks each.



Fig. S1 Ag NPs with a size distribution of (a) 5.0 ± 0.9 and (b) 7.8 ± 1.3 nm. Each panel consists of the experimental data (scattered symbol), two Gaussian peaks and overall fitting (solid lines).

Figure S2 shows SQUID magnetometry measurements of a Ag film collected ON-target onto NaCl and exfoliated with Kapton tape. The sample shows hysteresis which suggests that the observed ferromagnetism is independent of substrate as it rules out epitaxial driven formation or other such substrate-dependent processes.



Fig. S2 Room-temperature (300 K) *M* vs *H* loops for a ON-target Ag thin film transferred to Kapton tape after direct deposition onto a NaCl substrate. Inset shows full applied field range. Main graph is the zoomed section near the origin. Lines are guides to the eye.



Fig. S3 SEM images of ON- and OFF-target films. (a) ON-target deposition for 1 min and (b) 15 min. (c) OFF-target deposition for \sim 2 hr.

Estimation of the Ag/O ratio from MQCM data

Assuming all NPs are 3.3 nm in diameter (based on average experimental results of smaller NPs) and are perfect spheres, it can be estimated that each NP contains $N_{\rm ttl}^{\rm NP} = 1.50 \times 10^3$ Ag atoms (based on an atomic radius $r_{\rm Ag}$ of 144 pm).

The volume of the last atomic shell V_{OS} on a NP of radius r_{NP} can be estimated as

$$V_{\rm OS} = \frac{4\pi r_{\rm NP}^3}{3} - \frac{4\pi}{3} (r_{\rm NP} - 2r_{\rm Ag})^3 \tag{1}$$

from which it can be estimated that there are $N_{\text{surface}}^{\text{NP}} = 6.58 \times 10^2$ surface Ag atoms / NP. The total number of surface Ag atoms $N_{\text{surface}}^{\text{Ag}}$ in a 96.6 μ g Ag sample (containing $N_{\text{ttl}}^{\text{Ag}}$) is then given as

$$N_{\text{surface}}^{\text{Ag}} = \frac{N_{\text{surface}}^{\text{NP}}}{N_{\text{ttl}}^{\text{NP}}} \cdot N_{\text{ttl}}^{\text{Ag}} = 2.36 \times 10^{17}$$
(2)

Knowing this sample uptakes 0.7993 μ g of oxygen from QCM measurements (*i.e.* $N_{ttl}^{O} = 3.01 \times 10^{16}$) and assuming these O-atoms will react at the surface, the ratio of surface Ag atoms to O atoms is then

$$\frac{N_{\text{surface}}^{\text{Ag}}}{N_{\text{trl}}^{\text{o}}} = \frac{2.36 \times 10^{17}}{3.01 \times 10^{16}} = 7.84 \sim 8$$
(3)



Fig. S4 Peak assignments for the XPS survey spectra of O₂-kept and heat-treated Ag thin films.