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RESPONSE TO LETTER

Characterization of the Silver Nanoparticles in the Sovereign Silver and Argentyn 23 Bio-Active Silver Hydrosol Products [Response to Letter]

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Dear editor

This note is in response to the criticism vis-à-vis our paper "Comparative evaluation of commercial colloidal silver products" conveyed by Nan Qin, Paul Hemmes, and Kay Mitchen in their "Letter to the Editor". We are addressing below their comments and provide additional arguments reinforcing the validity of our findings.

The objective of our paper was to verify if the term "colloidal silver" was justifiably used in the case of 14 commercial products evaluated. The UV-Vis spectrophotometry, light scattering, and electron microscopy evaluations attested that Sovereign Silver, Argentyn 23, and seven other products did not contain silver nanoparticles and were improperly labeled "colloidal silver". The conclusion was strongly supported by the absence of a plasmon band, a convincing and widely accepted scientific argument the authors of the letter are dismissing.

The use of optical properties for detecting and characterizing plasmonic nanoparticles has been an integral and valuable part of colloid science for more than a century. In 1857, long before electron microscopy was discovered, Michael Faraday postulated that the ruby color of gold sols was caused by the presence of small dispersed metal particles.[1] In 1889, Carey Lea followed the same approach in studying colloidal silver.[2] Decades later, their findings based solely on the optical properties of the samples were confirmed by electron microscopy. As it provides simultaneously information about the *size, uniformity*, and *dispersion* of silver nanoparticles, UV-Vis has been recognized for long as the most versatile technique for evaluating silver sols. Since billions of particles in the light beam path are "interrogated" during the analysis, the information provided is far more representative for the sample than electron microscopy.

Despite the vast scientific evidence in favor or UV-Vis, the authors assert that it is unreliable because the SPR "changes" or "disappears" depending on size, surface chemistry, (and) aggregation. As we argue below, none of these factors are relevant in the case of their samples.

(a) According to all rigorous studies published, 2–10 nm particles like those shown in their micrographs *should display a plasmon band*. There is simply no credible mechanism through which particles of this size would disappear in the high purity water claimed by Natural Immunogenics as no species capable to dissolve them are present.
(b) "Surface chemistry" modifications can indeed affect the plasmon band. Again, since Natural Immunogenic samples contain only "pure silver and high purity water", no species that could interact with the silver surface and change it are present.
(c) Aggregation can cause plasmon "disappearance" only if it results in very large silver entities that settle. As documented in Table 1 in our paper, our preliminary protocol did not detect settlements in the case of the two Natural Immunogenics samples.

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In support of their assertions, Natural Immunogenics provides four citations we found to contain irrelevant information for the system in dispute.

- Citation 4 describes the appearance and disappearance of the plasmon band of 1.2 nm gold nanoparticles. The particles were exposed alternatively to oxygen and sodium borohydride to purposely oxidize the gold particles and then reduce the Au^{3+} ions formed. Nothing remotely similar can happen to Ag in the "high purity" Natural Immunogenics samples.
- Citation 5 (Raza et al) deals with silver nanoparticles imbedded in silicon nitride the changes in resonance being caused by excitation with electron beams.
- Citation 6 (Yang et al) deals with "thiolated Ag_{136} and Ag_{374} mega-clusters" in a very harsh chemical environment. These species have different optical properties than silver nanoparticles due to the thiol ligands bound to the surface which move them outside of the Mie theory governing silver nanoparticles.
- Citation 7 (Scholl et al) investigates the changes in the plasmon resonance of silver nanoparticles when interacting with high energy electrons in the TEM instrument.

It is puzzling why Natural Immunogenics chooses to trust these irrelevant studies and ignore the citations given in our paper in which recognized experts in the field state without equivoque that dispersed silver particles with sizes above ~0.45 nm *must display a plasmon band*.

We are pleased to see that based on the data presented in our paper Natural Immunogenics agrees now that Sovereign Silver and Argentyn 23 contain silver ions. This is in stark contrasts with the marketing materials for Sovereign Silver which state that it contains "only two ingredients: 99.999 pure silver & pharmaceutical grade purified water". Despite admitting that silver ions are present, Natural Immunogenics still insists that the majority of silver in the two samples is in form of silver nanoparticles. The UV-Vis data in our paper proves this is not true. In Figure 1 the absorbance of the two original samples was less than 0.01 in the 380 to 500 nm wavelength range. After adding a reductant, a plasmon band with an absorbance value of ~1.0 indicating the formation of silver nanoparticles appeared in both (Figure 6). Since the intensity of the plasmon band is proportional with the concentration of particles, the ratio of the two absorbance values (1.00/0.01) implies that the silver ions *represent at least 99%* of the total silver present. It is noteworthy that the UV-Vis method is able to detect concentrations of dispersed silver nanoparticles down to 0.1 ppm and even below if the path length is increased. Thus, even if only 1% of the total silver in the Natural Immunogenics samples would be in form of nanoparticles, *a plasmon band would be present*.

We disagree with the authors' assertion that the instrumentation used in the paper was not capable to "see" the silver nanoparticles they claim were present in their samples. Our STEM instrument had a resolution of 0.6 nm and thus the capability to easily visualize the 2–10 nm particles shown in their electron micrograph. We have our own reservations regarding the electron microscopy data submitted by Natural Immunogenics. As detailed below, they not only contradict their published claims but also raise questions regarding the rigor of analytical methods used and the veracity of the data.

(a) Based on the size bar, the majority of silver nanoparticles seen in Figure 1 are in the 2.0 to 10 nm range. This is in flagrant contradiction with the value of 0.8 nm ("the smallest in the world") advertised by Natural Immunogenics.
(b) According to any reputable study, silver particles in this size range must display a plasmon band. How could electron microscopy images be obtained if the UV-Vis does not show one?
(c) The AFM image in Figure 2 shows highly uniform silver nanoparticles with a claimed average size of ~0.8 nm while the TEM shows a broad range of particles from 2 to 10 nm. The two images cannot be reconciled and seem to depict two different products.
(d) The ~0.8 nm particle size assigned by AFM analysis is scientifically dubious as the reported uncertainty of AFM measurements is ~0.75 nm.[3]
(e) Assigning a size value based on the "chopped" height distribution shown in Figure 2 cannot be justified scientifically. Clearly, the capability of the method does not extend below 0.85 nm and a reliable average value cannot be determined based only on half of the distribution curve.

In conclusion, we stand firmly by the investigation methodology, results, and conclusions presented in our paper.

Disclosure

Dan V. Goia is an Emeritus Professor at Clarkson University, Potsdam, NY 13699 and an independent consultant in the field of fine metallic particles. He is the inventor of Coated Silver, one of the products included in the study. Dr. Ajeet Kumar reports no conflicts of interest in this communication.

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