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A Multi-Size Study of Gold Nanoparticle Degradation and Reformation in Ceramic Glazes

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Abstract

Most traditional ceramic glazes employ high amounts of transition metal colorants that are toxic to the environment and can cause health issues in humans through surface leaching. Gold nanoparticles (Au-NPs) have been found to be environmentally friendly and non-toxic alternative metal colorant in ceramic glazes. The plasmon band observed with Au-NPs can result in vibrant solutions by manipulating NP size, shape, and concentration; however, the effects of traditional firing in both reductive and oxidative kilns on Au-NPs are poorly understood. Aside from ancient art processes whose mechanisms have not been fully explored, the use of Au-NPs as suspended ceramic glaze colorants remains somewhat unexplored. Au-NPs have been previously reported to diminish in size during sintering and possess significant differences in concentration with respect to reduction and oxidation firing atmospheres. As a means of studying possible degradation/re-nucleation processes within the glaze during firing, a systematic study introducing different diameter Au-NPs into the glaze materials was conducted with transmission electron microscopy and reflectance spectroscopy used to probe possible mechanisms which showed changes to Au-NP diameter and color intensity, making this work applicable to industry and art current practices.

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Keywords

gold nanoparticles, ceramics, glazes, firing, reduction, oxidation, surface plasmon resonance

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I. Introduction

Apart from their wide-spread use in heterogeneous and homogeneous gold catalysis,[1, 2] and sensing platforms/materials,[3, 4] gold nanoparticles (Au-NPs) have also been utilized in artisan coloring applications for a decorative coatings on ceramic surfaces. More specifically, Au-NPs have been employed as decorative coatings on top of ceramics both as an underglaze stain and as enamels/inks such as the Purple of Cassius [5, 6] Au-NP based color is achieved via a collective interaction of light with these materials known as surface plasmon resonance effect.[7, 8]. The ability to manipulate numerous variables during NP synthesis allows for a versatile coloring system for ceramic and glass surfaces. [9, 10]Through surface plasmon resonance, NPs allow for varying colors, intensities, and coloring effects by manipulating characteristics such as size [11], morphology [12], and concentration [13]. The manipulation of these characteristics has been demonstrated by changing the environment during synthesis [14], pH [11, 15], size of starting growth seed [12], and concentrations within the solutions [16]. By modifying these conditions during the synthesis, NPs can be engineered to possess a wide variety of optical properties. The predominant usage of these Au-NP materials has been as a decorative application on top of glass and ceramic surfaces that have been previously cured and then undergo a subsequent third firing to seal the Au-NP stain.[10, 17] While this type of application has been widespread, a largely unexplored application is the introduction and suspension of Au-NP material within a ceramic glaze that is applied prior to firing in kiln equipment typically found in art studios.

Traditional ceramic glazes typically include high amounts of toxic elements including Co, Pb, Cd, Ni, Cr, and Mn and have been previously reported to be responsible for a number of health and environmental problems [18, 19]. These traditional glazes often contain anywhere from 4% to as high as 12% of a loading metal for color or visual effect purposes [20]. For example, dark green ceramic glazes often require a mixture of 5-10% cobalt and chromium; Prussian blue requires 5-10% cobalt and manganese; orange red requires 1-4% cadmium and selenium; reds can contain 5-8% nickel [20] – a known carcinogen. High levels of lead- and cadmium-leaching have also been observed from traditional ceramic glazes on both antiques [21] and modern dishware [22, 23]. Lead-leaching levels that exceed the FDA allowance have been observed by exposure to both 4% acetic acid, the standard test established by the FDA, and everyday mildly acidic foods including pickle juice and orange juice. To that end, gold-based coloring systems are an attractive potential alternative to these metal colorants.

As previously mentioned, gold has been used in the past as third firing application ink over pre-fired glazes [5, 10, 24] but, to our knowledge, is virtually unexplored as a pre-firing colorant that is incorporated within glaze matrices and fired with common art studio equipment. In 1960, a rare example of the use of colloidal gold within a glaze formation specifically emphasizes the difficulty of using the material in this manner, concluding a lack of repeatability as well as a poorly understood mechanisms and controls for certain antiquated recipes.[6] Our laboratory previously reported the successful incorporation and suspension of Au-NPs within a pre-fired glaze at significantly reduced metal loadings compared to traditional metal-based glaze recipes (0.015% to 0.1%). Fired with typical art studio equipment in both oxidative and reductive environments, certain Au-NP glazes not only produced color intensity comparable to that of traditional loading metals but also was shown to be more resistant to metal-leaching than ceramic glazes with traditional loading metals (Provisional Patent Application #15/790,717) – making the Au-NP based glazes less cytotoxic to humans [25]. While this study further demonstrated Au-NPs to be a versatile tool in ceramic glazes, it also revealed interesting but poorly understood Au-NP morphology changes during the firing process. Post-firing glazes clearly showed Au-NP content with TEM analysis, but their average diameter significantly decreased: 12 nm diameter Au-NPs incorporated into the pre-fired glaze recipe were reduced by half after firing in both reductive and oxidative environments [1]. Additionally, the results of that study suggested that, while glazes fired in reductive and oxidative environments each showed Au-NPs were present post-firing, glazes from the former material possessed a significantly larger number of Au-NPs, a property resulting in a notable difference in coloring effects as measured with reflectance spectroscopy. This apparent coloring difference being attributed to Au-NP concentration differences is consistent with other studies examining color intensity with respect to pigment volume via reflectance spectroscopy and colorant volume examination. [26] While the effect has been clearly observed in these past studies [14], the mechanism that produces the effect, the Au-NP degradation/formation within the glaze matrix during both oxidative and reductive heat treatments, remains largely unexplored.

In this paper, the mechanism of Au-NP degradation and reformation within a ceramic glaze coating, during firing in oxidative and reductive kiln atmospheres is explored via the suspension of multi-sized Au-NPs within ceramic glaze materials. A better grasp of Au-NP formation mechanisms during firing could lead to greater control in firing conditions and would lend itself to superior color quality and less material consumption. While the Au-NP effects observed in this study do not represent final quality colors, they provide a means explore the mechanisms of particle formation and degradation. Gaining such insight would allow for low toxicity metals such as gold to find use in studio-safe production of glazes that are free of cadmium, a known toxic colorant.[21] Additionally, establishing gold as a model to probe the mechanism of plasmon resonance in glazes, allows for a more developed understanding of NP degradation, nucleation, and growth mechanisms during sintering. An increased understanding of these phenomena could allow for the use of other metal nanoparticle suspensions, thus creating a wider range of options for more environmentally and economically friendly ceramic coloring systems, including (CdSe)ZnS [27], Ag [11, 28], Si [29], ZnO [30], and TiO_2 [31].

II. Experimental Section

II.1: Materials

Gold (III) chloride trihydrate (>99.9%), sodium borohydride (99%), sodium citrate tribasic dihydrate (≥99%), and ascorbic acid were purchased from Sigma Aldrich. Cetrimonium bromide (CTAB) (99.52%) was purchased from Chem-Impex Int'l Inc. All raw glaze materials were purchased from Clayworks Supplies in Richmond, VA, and used at the Visual Arts Center of Richmond. Clay (Laguna Clays, Little Loafers) was formed into tiles and used as a ceramic substrate, throughout. All glassware was cleaned with aqua regia (3:1, HCl/HNO_3). *Warning: Aqua regia is a very strong acid; extreme caution should be used when handling or storing this material.* All solutions were made with 18.0 MΩ·cm nanopure water.

II.2: Multi-sized Nanoparticles Synthesis

Multi-sized Au-NPs were adapted from Jana, et al, and synthesized using strategic variations of the NP synthesis procedure through seeding and proliferation. Solutions and sizing analysis were consistent with previously reported Au-NPs [12, 32]. A 300 mL, 1.0 mM growth solution of $HAuCl_4$ was prepared with 7.5 g of CTAB serving as the capping agent. The solution was heated until the CTAB was fully dissolved, and the solution turned a dark, translucent orange. The growth solution was allowed to cool to room temperature before use. While cooling, solution of 0.1 M ascorbic acid (10 mL) was prepared as a reductant. A 20 mL seed solution was made from 1.0 mM $HAuCl_4$ and 1.0 mM trisodium citrate in an Erlenmeyer flask. Once the growth solution reached room temperature, 1.0 mL of chilled (~0°C), 1.0 mM $NaBH_4$ solution was immediately but slowly added to the stirring seed solution which changed from light yellow to dark purple, an indication of NP nucleation.

Three different Au-NP batches (A-C) were synthesized which resulted in incremental nanoparticles sizes. For batch A, 99 mL of growth solution was combined in an Erlenmeyer flask with 1.5 mL of ascorbic acid solution while stirring. The color of the solution changed from dark orange to light yellow to clear, which indicates the reduction of gold atoms. Next, 11 mL of seed solution was immediately added to batch A while stirring vigorously for 10 minutes. A color change was observed from clear to wine red. The solution was allowed to rest for 20 minutes prior to obtaining an aliquot for batch B. Batch B followed the same procedure as batch A except 11 mL of batch A (aliquot) was used instead of the seed solution. The final color of batch B was purple-brown. The solution was allowed to stand for 20 minutes before a sample was obtained for batch C. Synthesis of batch C followed the same procedure as batches A and B, but with 11 mL of batch B used as the seed solution. Final solution color was an opaque medium brown. All solutions were analyzed with TEM and covered in aluminum foil to prevent aggregation until use.

II.3: Glaze Synthesis

After multi-size Au-NP sizes were verified by TEM, the multi-size NP solutions were centrifuged at 10,000 rpm for 90 minutes and roughly three quarters of the solutions' supernatant was poured off to produce more concentrated nanoparticle solutions. Each multi-size Au-NP solution was added to 80.0 g glaze batches that are formulated to be ceramic-compatible with respect to expansion-contraction coefficients as a borosilicate glass glazes. These consist of 20% Kaolin EPK, 19% silica, 6% talc, 20% frit 3134 (which is 22.8% B_2O_3 content), 15% wollastonite, and 20% G-200 feldspar, which is an adaptation from the "five 20s" common glaze recipe. As is common with ceramic studio culture, standing ceramic and glazing practices was employed to better adapt these techniques to art studio settings. To that end, ceramic tiles were dipped into a raw materials glaze suspensions (in water), described above, held for 3 seconds, withdrawn from the mixture, and allowed to dry prior to firing. Glazes were then were fired in either reductive or oxidative environments to cone 10 (2345 F, 1286 C) and 6 (2200 F, 1200 C), respectively, to retain consistency with modern firing practices.

II.4: Post-Firing Glaze NP Analysis

After firing in both reductive and oxidative atmospheres at cone 10 and 6, respectively, samples were analyzed using an Ocean Optics Halogen lamp (HL-2000-FHSA) and Flame miniature spectrometer (FLAME-S-VIS-NIR-ES, 350-1000 nm) to quantify the produced colors by percent reflectance. Glaze color was observed to be continuous throughout the sample, suggesting nanoparticle suspension throughout the glaze and not just a surface presence, **Fig. S2**. Glaze from each sample was then obtained from the back of tiles with a Dremel. The glaze dust was processed for 2 to 3 minutes with a mortar and pestle or until the ground material was a fine powder. The powder was transferred to a vial and suspended in ethanol. Samples of each (5.0 μL) suspended solution were placed on 400-grid, copper TEM grids with carbon film for analysis. Images were obtained for each sample until greater than 100 particles were observable, such that statistically relevant sizing analysis could be performed. Mortar and pestle were rinsed thoroughly with ethanol and water between each glaze sample.

III. Results and Discussion

A popular method of synthesizing Au-NPs is through the Turkevich method which involves combining $HAuCl_4$ with sodium citrate, which acts as both a reducing and capping agent [33]. When gold atoms are reduced, they begin to nucleate into Au-NPs (i.e., nucleation) and then expand as more gold atoms attach (i.e., growth). Once a certain diameter of NP is achieved, a capping agent (e.g., citrate, alkanethiol) surrounds the NP, preventing further growth. For use in a ceramic glaze, the Au-NP solution prepared with citrate stabilization [12] in this way is then combined with dry glaze ingredients before firing, such that the NPs are suspended in the glaze solution. Prior to suspension in the glaze solution, the Au-NPs were characterized as traditionally reported in the literature: UV-Vis spectroscopy of the colloidal suspension and TEM for sizing analysis. Results were typical for these materials and have been extensively reported, including a similar spectroscopic signature surface plasmon band and average Au-NPs diameters of 20 nm (**Figure S1**). [12]

The synthesized Au-NPs were incorporated within the glaze material and coated on three sets of tiles prior to firing in both reductive and oxidative environments. More specifically, glazed tiles were then fired in either a "reduction" kiln that employs the use of natural gas or liquid propane, with variable access to air to control reductive atmosphere during sintering or a nichrome-wire "oxidative" kiln operating with air ventilation during heating. After firing, the cured glaze from the reductive kiln exhibits a deep red color (**Fig. 1A**) comparable both visually and spectroscopically to metal-based colorants within similar glaze recipes – i.e., similar reflectance profiles to traditional metal-based glazes (**Figure S2**). The observed coloring is attributed to the presence of Au-NP in the post-reductive kiln fired glaze and, importantly, is not isolated to a surface phenomenon. A microscopic cross-sectional analysis of a glazed tile (**Fig. 1A-inset**) shows that the glaze coating the ceramic understructure is uniform in color from the outer surface to the ceramic interface. Moreover, as previously shown, TEM analysis of the glaze reveals the presence of suspended Au-NPs post-fired glaze.[14] Of particular interest, TEM analysis of the tiles from the oxidative kiln also show the presence of Au-NPs in the glazes but the same coloring effect is not observed. While this provides some information about particle size changes during firing, the mechanism of degradation and/or re-nucleation and growth of Au-NPs, the changes that they undergo during both reductive and oxidative kiln firing, has not been explored.

Metal components within traditional glaze mixtures, such as Sn, are possible reducing agents during firing such that, if there is ionic gold stemming from Au-NP degradation during firing, nucleation from its reduction could occur. [5, 9] In order to test this possibility, Au-NP glazes (0.050% Au) [14] were prepared both without and with the addition of 4.0% SnO_2 as a sacrificial reductant and opacifier. After the reduction firing of two samples of glaze, no visible difference in color profile could be observed, **Figure 1A**, with only slight, negligible differences in particle size, **Figure 1B**.[14] Similar to a previous study, particle diameter was observed to decrease during firing from original size averages for both neat and 4.0% SnO_2 additive samples. This was surprising, as gold nanoparticles are commonly observed to grow in diameter upon heating[34]. This phenomenon could be related to a pattern observed in a recent study with tin oxide supplied as a reductant, such that the absence of tin resulted in fewer, but larger particles,, similar to oxidization-fired samples in this work.[9]

III.2: Multi-sized Nanoparticle Synthesis

Multi-size Au-NP synthesis yielded three different Au-NP diameters (**Figure 2**), differing by ~20 nm in each case. Batch A yielded Au-NPs with diameters of 21.0 ± 3.0 nm (n = 100). Batch B yielded Au-NPs with diameters of 38.7 ± 3.4 nm (n = 100). Batch C yielded Au-NPs with diameters of 57.5 ± 10.5 nm (n = 100). Batches B and C contain some few rod formations, which were not included in these measurements. Minor formation of rods is consistent with the literature and particle synthesis analysis [32].

III.3: Nanoparticle glazes fired in different environments

Au-NPs glaze samples were fired in a reduction kiln along with other normal pottery at the Visual Arts Center of Richmond (Virginia). The reduction-fired work was loaded in a kiln that was allowed to reach 1000°F (538°C) for a candle time of twelve hours before significantly increasing the rate of firing. The kiln was then gradually ramped up to cone 10 at 2345 °F (1285 ºC) over eight hours. Finally, the kiln was allowed to cool for 24 hours before removing the samples. All three multi-size NPs batches produced glazes that were a dark red-purple (**Fig. 3, left tiles in sample images**). Glaze samples were obtained, processed, and analyzed via TEM imaging and sizing analysis performed on 100 individual nanoparticles for each batch (i.e., n = 100). Sizing analysis from glaze samples prepared with batch A yielded particles sizes of 16.6 ± 13.4 nm suggesting a large range of particle sizes – likely due to degradation, renucleation, and growth. The histogram is suggestive of a large number of smaller particles with retention of some larger NPs. Batch B yielded particle sizes of 14.9 ± 4.3 nm (**Fig. 3, center**). Batch C yielded particle sizes of 13.4 ± 5.4 nm. Although starting batch sizes were all normally distributed, batches A and C demonstrated somewhat low-diameter-favored distributions after firing. Batch B's distribution remained more normal.

Oxidation samples were fired in nichrome-wired electric kilns to cone 6 at 2200°F (1200 ºC) on a medium setting. The kiln was then allowed to cool for 24 hours before the samples were removed. The glaze samples fired in oxidation kilns produced less visibly intense colors, suggesting a significant decrease in NP concentration. Consistent with this phenomenon, the MS Au-NP glazes produced light pink hues for all three batches (**Fig. 3, right tiles in sample images**). Glaze samples were obtained from all tiles, imaged via TEM, and particle sizing analysis performed on each sample (n = 100). Batch A yielded particle sizes of 5.4 ± 0.7 nm. Batch B produced particles of size 15.1 ± 4.8 nm. Batch C produced particles of size 24.2 ± 8.2 nm (**Fig. 3, right**). All three batches had normal size distributions for samples produced in the oxidation atmosphere via histograms. Glaze samples produced from batch A were comparable to the particle sizes in the first study, which is consistent for the starting approximate size [14].

These glaze results offer an interesting perspective into firing mechanism, reductive/oxidative environment, particle degradation, nucleation, and growth. From changes in average particle diameter to large standard deviations in particle size, and differences in color intensity, all of these communicate mechanistic information for different thermal and nucleation/growth effects during firing. For glaze samples produced with batch A NP, particle sizes from the reduction environment have a somewhat large standard deviation of particle diameter, but the final average size (16.6 ± 13.4 nm) is lower than the reported starting sizing (21.0 ± 3.0 nm). After firing in the oxidation atmosphere kiln, glaze samples from batch A NP contain average NP diameters that are lower than both original and reductive samples, suggesting more degradation than that of the reductive conditions. In batch B, the particle sizes in reductive and oxidative atmospheres were statistically similar (14.9 ± 4.3 nm and 15.1 ± 4.8 nm, respectively), suggesting some overlap in degradation and growth mechanism, despite starting at 38.7 ± 3.4 nm. In glaze samples prepared from batch C NP, the average particle diameter from the oxidation kiln (24 ± 8.2 nm) is larger than those fired in a reduction atmosphere (13.4 ± 5.4 nm), though presence of some larger particles are visible in the histograms. Again, this is surprising, as particle size is expected to increase with respect to temperature via Ostwald ripening.[34] However, some studies have demonstrated particle stability to exist beyond vitrification temperature and particle size to be a function of available reductant, even at elevated temperatures.[9] This may suggest that particle surface degradation takes place in both atmospheres as a function of heat, but a reduction atmosphere allows for re-nucleation and growth of new nanoparticles, such that the average particle diameter is statistically shifted lower (more new, small particles). Conversely, an oxidizing atmosphere would likely possess more degradation effects, significantly fewer new nucleation and particle growth events, and thus no statistical shift in particle diameter average would exist.

The reduced samples of all three batches resulted in similar average particle diameters and resulted in roughly equivalent color profiles (**Fig. 3**) – with a large number of particles in the 10 nm range. Interestingly, Au-NP retention was achieved without the use of tin oxide, as it was demonstrated to be unnecessary for glaze color from a previous study.[14] Additionally, it has been observed that AuNP are not absorbed in a molten glass until roughly 1400 °C, significantly above our firing temperature.[9] This is suggestive of re-nucleation and growth during firing in a reductive atmosphere after surface degradation from heat. Similarly, another study has demonstrated variations in particle concentration and size as a function of available reductant, albeit tin, in highly controlled settings.[9] In a gas-reduction-fired kiln, diminished oxygen levels in the kiln allow for incomplete combustion, yielding high concentrations of carbon monoxide. The accepted mechanism for ceramic glaze reduction is such that formed carbon monoxide (CO) strikes the surface of a ceramic body, abstracts oxygen from the surface of the glazes, forms CO_2, and reduces the ceramic/glaze surface [35, 36]. While heat during firing could possibly allow for the degradation of NPs at elevated temperatures, this reductive atmosphere could allow for the reduction of free, degraded Au atoms, nucleation, and reformation into NPs (small diameter) via growth. The reformation of new nanoparticles in a reductive firing would provide for smaller but more abundant Au-NPs in the glaze, which would make for consistently vibrant colors regardless of starting NP size.

In the oxidation kilns, the oxygen-rich atmosphere promotes a more purely oxidative atmosphere, as air is drawn through the kiln during sintering. The oxidation-fired samples would undergo particle degradation as a function of heat work, much like the reduced glaze samples, with respect to surface Au-NP atoms. While CO reduction is likely not taking place, some small degree of getter reduction is possible. A significantly weaker force in promoting reduction, getter reduction allows for reduction of some glaze component or ceramic substituents through a sacrificial substance, the "getter," and thus some transfer of electrons is possible. Getter materials are typically placed near the material that is to be reduced during heating or mixed in with ceramic material. This allows for electron transfer from the sacrificial getter material to the reduced material [37]. Getter reduction may explain why some nucleation and growth is seen in oxidative firings. Impurities within the ceramic or glaze can act as getter materials, which could allow for some degree of reduction of Au atoms and formation of NPs. In an oxidative environment, larger NPs are observed on average, contributing to a larger average particle diameter as compared to the reduction-fired Au-NP glaze samples. Overall, the apparent lower nanoparticle concentration accounts for less vibrant colors after oxidation sintering.

III.4 Color Profiles

Reflectance spectra were obtained from the glaze samples (prepared from various sized Au-NP and fired in reductive/oxidative environments) mentioned above, in **Fig. 4**. Percent reflectance has a reciprocal relationship with color intensity; darker samples demonstrate a lower reflectance profile and a somewhat more pronounced reflectance color band, while lighter samples demonstrate a higher reflectance profile across the visible spectrum, as more total light is being reflected off of samples with individual color bands being less pronounced. The concentration of NPs in these glazes can be directly correlated to color reflectance due to the surface plasmon resonance of the Au-NPs. As the concentration of Au-NPs increase, the intensity of color increases (Supporting Information, S3). Via a reflectance measurement, the darker, reduced glazes have lower reflectance magnitude due to higher light absorbance, which yields more deep, saturated color. Additionally, the lighter, oxidized glazes demonstrate higher reflectance measurements due to less light absorption, which is indicative of a lower particle concentration. It should be noted that reduction-fired samples demonstrate comparable reflectance color profiles to traditional red glazes with significantly higher metal colorant loading, **Fig. S2**.

Due to the surface plasmon resonance of Au-NPs, a higher concentration of Au-NPs within the silicate matrix would correspond to greater light scattering and for the glaze to reflect a "richer" color. To that end, a more defined and concerted reflectance peak (and not bulk, broad, high reflectance across the visible spectrum) can infer Au-NP concentration within a glaze. Additionally, the renucleation, growth, and statistical decrease of average particle diameter through more NPs in the silicate would result in darker surfaces, observed here. For oxidized samples, one would expect degradation and oxidation of Au-NP without substantial renucleation and growth to result in diminished NP concentration, diminished color intensity, less saturated color, and more broad/higher reflectance consistent with these measurements – which is observed by a difference of 30% reflectance in **Fig 4**.

III.5: Sizing Comparison of Nanoparticle Systems

When comparing sizing patterns of these systems, different trends are observed between reduction- and oxidation-fired samples. **Fig. 5** illustrates the trends in particle size before and after firing from original particle sizes first reported by Lambertson (Batch O) and those reported in this work. Though an increase in particle diameter was employed, final particle sizes are diminished, with a decreasing size relationship for reduction-fired particles and an increasing size relationship for oxidation fired particles. This phenomenon may exist due to heat degradation of surface Au atoms, renucleation, and growth of Au-NP during reduction firing, resulting in a diminished average particle diameter, mentioned above. Both reduction and oxidation atmospheres show diminished average particle size, consistent with NP degradation for all four samples and independent of starting average diameter. Despite starting with incrementally sized particles, the average diameters of the reduction-fired MS NP samples were all statistically similar to each other. The oxidative atmosphere, conversely, produces particles with diameters that are more relative to their original starting size for Batch A. As the starting particle size increases, the final particle size after firing becomes larger compared to previous batches. This phenomenon is consistent with the mechanisms proposed above. As an oxidative atmosphere would not promote significant re-nucleation and growth, the reduced Au atoms nucleate and grow to shift statistical averages down – with oxidative samples possessing larger particle diameter averages. The similar color profiles of the oxidized MS NP samples in **Fig. 4** and increasing particle sizes in **Fig. 5** suggest that color intensity is dependent on the concentration of the Au-NPs, not necessarily size for oxidation-fired glazes. Based on intensity of color and lower reflectance measurements of the samples, this is suggestive that batches O and A have the smallest particles and thus appear to be in a greater abundance within the glaze after firing. Similarly, batch C has the largest particles but fewer NPs overall – demonstrating less intense color in **Fig. 3c**.

V. Conclusion

This study supplies new nanoparticle size information about potential particle degradation and growth mechanisms in commonly found art studio kilns. As such, particle sizes are observed to diminish, and to different degrees, as a function of reductive or oxidative atmosphere of the kiln. This is suggestive that the intense heating of the kilns and reductive nature of the atmosphere can contribute to nanoparticle degradation, despite the robust nature of Au-NPs. While this mechanism is still not understood, it provides more information about the creation of surface plasmon resonance color in commonplace, art studio equipment, which would eventually allow for low metal loading color efficiency in art studios, worldwide. By observing and better understanding atmosphere and heating effects on Au-NPs in ceramic glazes, kiln firing procedures can be optimized to potentially allow for new, low-metal color profiles comparable to traditional glazes.

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