TECHNO FILE

silver and gold

by Karthik Lalwani, Micheal Leopold, PhD, and Ryan Coppage, PhD

Silver and gold have long had their place in the ceramics and glass world—and not because of the metallic colors they are known for. Both metals readily form nanoparticles during reduction firings (and gold in mid-range oxidation firings) that can be suspended in glasses and glazes to create unique colors.

Defining the Terms

Electrons: The subatomic particles of an atom, which flow freely in metals, allowing for current or conductance, and allow for surface plasmon resonance light properties to exist.

Nanoparticle: A small particle between 1 and 100 nm in size, which often interacts with light through plasmon resonance to create various color phenomena.

Reduction Potential: The electromotive potential required or released when a positively charged atom accepts electrons and is reduced to a less positive state. For example, Au^{+3} can reduce to Au^{+1} or Au^0, both of which have different reduction potential values.

Spontaneous Reduction: A positive reduction potential is associated with negative Gibbs free energy through the free energy to cell potential equation: $\Delta G°cell = -nFE°cell$. As such, any positive reduction potential is considered spontaneous as it happens freely and releases energy. The more positive the value, the earlier in line it is to undergo reduction from available electrons. Gold will reduce before silver when comparing reduction potentials.

Surface Plasmon Resonance: The phenomenon of light striking a small metal particle, exciting electrons on that surface, and electrons oscillating around the particle, such that their oscillation energy (controlled by diameter) is responsible for the wavelength of light absorbed (and thus their color).

Transmission Electron Microscopy (TEM) or Microscope: A high-end microscope in which, instead of focusing light, a series of electromagnets focus an electron beam generated from a filament at the top of an instrument to image materials on the nanometer scale—with dimensions on the scale of 1×10^{-9} meters.

Zero Valency: Atoms in their natural state, having an equivalent number of electrons and protons, and thus a zero charge. This is often metal in its most natural, elemental state.

Gold Pinks and Reds

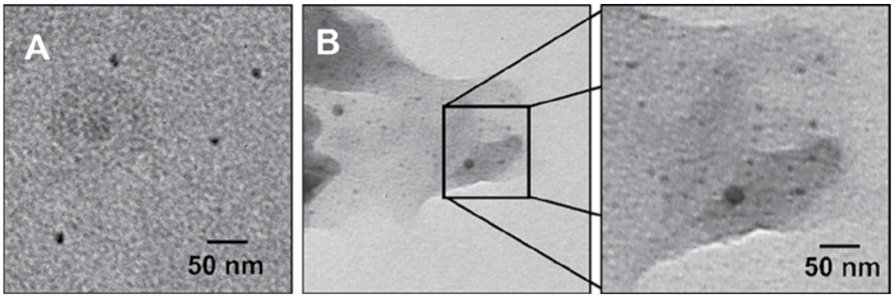
Simply put, there are a number of us in the science world who are nanomaterial chemists. It's a strange little section of chemistry that doesn't properly fit into any of the classic five disciplines—organic, inorganic, analytical, physical, and biochemistry. As such, our kind have strange training that is part inorganic chemistry, part analytical/instrumental chemistry, and a decent part applied physics. We make things work with respect to physical phenomena—but on a nanoscale level—on the order of 10^{-9} meters. Fortunately for us, this is where a lot of light mechanisms also happen to exist.[1] If you were to pair up a nanomaterials chemist with any system that incidentally employs nanoparticles for color, they'd eventually recognize a synthesis recipe and point it out. And, arguably, that's what a handful of glazes actually are—nanoparticle syntheses that are stabilized in glass—but on the surface of a beautiful piece of pottery.

The September 2021 Techno File article, "Copper Red Nanoparticles," touched on copper,[2] but now the focus is on silver and gold—slightly more expensive (the quantities used literally translate to about 40 cents/mug), but also responsible for unique color in the ceramic glaze world. At right (1), a minuscule amount of gold was added to a clear glaze base and fired in both reduction and oxidation environments to give a soft salmon pink and deep red color, respectively. The color results from nanoparticle surface plasmon resonance.

1 Roughly 40 milligrams (0.0394 grams) of gold chloride, suspended in a 100-gram sample of Ron Roy's clear base, and fired to cone-6 oxidation, left, and cone-10 reduction, right.

Nanoparticle Formation

Gold is one of the most stable metals on the periodic table, with a spontaneous reduction of $Au^{3+} + 3\,e \rightarrow Au^0$; this equates to a positive reduction potential of +1.40 volts. Gold undergoes this spontaneous reduction so aggressively that a stainless-steel spatula will dissolve when placed into a bottle of $HAuCl_4$ (chloroauric acid) and contaminate the whole bottle. Essentially, gold will steal electrons from most other elements to form zero-valent gold. When gold is mined, it exists naturally as its bright gold metallic color, often in granite and quartz veins. Conversely, silver, with its reduction potential of +0.80 volts is more easily oxidized. When mined, it appears black—as silver oxide or silver sulfide—just as your silver jewelry and flatware



2 TEM images of gold nanoparticles. A) A sample of gold nanoparticles from an oxidation-fired glaze that corresponds to the left tile in figure 1. B) Gold nanoparticles (from figure 1, right tile) embedded in a shard of glaze (middle), in which the nuclear density of the gold scatters more electrons from the TEM and shows up as dark portions of the image and the silica matrix of the glaze is gray from minimal electron scattering. Right, an expanded section of the glaze.

tarnish over time. Not surprisingly, due to how readily it spontaneously reduces, gold nanoparticles form almost effortlessly in many color applications, medical therapeutic, or detection and delivery systems.[3] They form in both oxidation and reduction environments, as evident in figure 2. However, they are present in different concentrations, as the color intensities are quite different in figure 1.

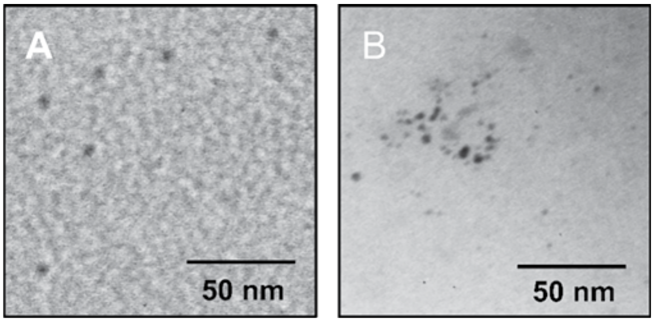
This phenomenon dates back to stained glass, a specific example is the Lycurgus cup,[4] but has rarely been used in ceramic glazes, despite its vibrant colors. Unbeknown to ancient Romans, silver-gold-copper alloy nanoparticles were forming in their stained glasses from their inability to separate and purify the noble metals. With modern technology and purifying techniques, recent efforts have been made to recreate these colors in standard firing practices.[5]

Silver: The Problem Child

To be perfectly candid, I have been chasing silver nanoparticles in mid-range oxidation kilns for roughly two years. I can get them to form, even in the presence of silicon carbide, but not in high enough concentrations to replicate the color that shows up in reduction kilns—in which a constant stream of carbon monoxide prevents them from oxidizing back into their Ag$^+$ (the ion form of solid silver) state. And upon imaging the glaze via TEM, our group has found that they are only stable if imaged within about 30 minutes or so of being ground out of their glass encapsulation—and then the particles oxidize and fall apart in air (on the TEM imaging grid).

These silver nanoparticles make for truly unique colors in reduction firings—sage greens that don't exist otherwise as they aren't produced with traditional green colorants like chromium oxide, copper carbonate, or copper oxide. While some silver particles are found in the oxidation-fired tests (figure 4), they do not possess sufficient color from the plasmon resonance phenomenon, as seen in figure 3.

3 Color results from 0.50 grams of silver nitrate, suspended in a 100-gram sample of Ron Roy's clear base, and fired to cone-6 oxidation, left, and cone-10 reduction, right.



4 TEM images of silver nanoparticles, including: A) from an oxidation-fired sample that corresponds to the left tile in figure 3, and B) from a reduction-fired sample that corresponds to the right tile in figure 3.

What It All Means

Most glazes achieve color through crystal field theory and use more net colorant, whereas nanomaterial systems express color more efficiently, whether copper, silver, or gold. And though these systems have been used unintentionally for hundreds of years, control over the parameters and color effects are just now being realized.

Silver nitrate is readily available across most of the Internet. You can also take old silver jewelry and dissolve it in nitric acid and then let it evaporate/softly cook it off to obtain its silver salt—AgNO$_3$. Gold is trickier. An old unpaired gold earring can be dissolved into a mix of hydrochloric acid and nitric acid (aqua regia) to form the gold salt (HAuCl$_4$). There are a lot of Internet resources for doing both of these processes. **Note:** Follow recommended safety precautions and use protective equipment when handling and storing acids.

RON ROY BASE

Cone 6 Oxidation/Cone 10 Reduction

Talc	6.00 %
Wollastonite	15.00
Ferro Frit 3134	20.00
Custer Feldspar	20.00
EPK Kaolin	20.00
Silica	19.00
	100.00 %
Add: Silver Nitrate	0.50 %
or Gold Chloride	0.04 %

To achieve good color results, thicker application is better, as this glaze is incredibly stable and does not run much. If firing in oxidation, a medium firing ramp with a 15-minute hold at the top temperature is sufficient to let any off-gassing pinholes seal over.

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