APPLICATION OF NANOMATERIALS IN THE CERAMIC BODY, GLAZES AND GLASS IN THE HISTORICAL PROCESS

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DOI: https://doi.org/10.5281/zenodo.7083296

Abstract
Nanoscience is about the occurrence in systems with nanometer and it expresses 10^{-9} times smaller than the unit. Scientifically, it was first defined by Richard Feynman in 1959 and then sprang into the public consciousness in 1982 (Lindsay, 2009). Today with the development of technology, use of nanoscale materials has become very common in the manufacturing and material sectors, medical and health sectors, in aerospace research and in many fields. Apart from science, the use of Nano-dimensional materials in arts, especially in ceramics and glass art, is well known from the Bronze Age up to the present. The use of Nano-sized coloring metal oxides in the ceramic and their glazes also glass fragments found in excavation was determined by different analytical methods such as XRD, TEM, and Raman (Colomban, 2009). The most distinctive feature of the use of Nano-sized metal oxides in glass and glaze construction is the color change of these materials with light change. This is due to the dimensional properties of the metal oxides. As an illustrative example, the Lycurgus glass cup produced in Rome in the 4th century or ancient luster glazes are some of the materials which their colorant is a Nanosized metal oxide. The use of Nano-sized materials, especially metal oxides is in order to reduce the sintering temperature of the ceramic body and create different artistic effects with glazes is continuing up to the present day. In this study, the use of nanostructures in the production of ceramics from ancient times to the present day will be researched by different analyzes on samples.
Keywords: Artistic glazes, Nanotechnology, Nano metal oxide, ceramic body, colored glass.

Introduction

Nanoparticle and properties of this scale of materials are a universal challenge for today's technology and the near future observations of science. Usage of nanomaterials traces back to traditional Chines medicine (Vajtai, 2013), Mayan (José-Yacamán, Rendón, Arenas, & Puche, 1996), (Schodek, Ferreira, & Ashby, 2009) and Medieval Italian paints (Fig. 1).

Fig.1, Mayan mural painting from Cacaxtla, Mexico. The intense blue results from an amorphous silicate substrate with embedded metal and oxide nanoparticles on the surface (Schodek et al., 2009).

Nowadays nanotechnology more or less contain almost all of science and manufacturing technologies such as materials and manufacturing, medicine and health, aviation and space exploration, biotechnology and agriculture, and many other areas. As an ıllustration nano-pigments have recently acquired a wide range of industrial applications in automobile coatings, plastics, etc.(Hu, Xue, Zhang, Sheng, & Liu, 2008). For instance, in cosmetic applications, TiO_2 and ZnO are being improved for use in sunscreens, in order to prevent skin damages caused by sunlight radiation (Serpone, Dondi, & Albini, 2007) (Fig 2).

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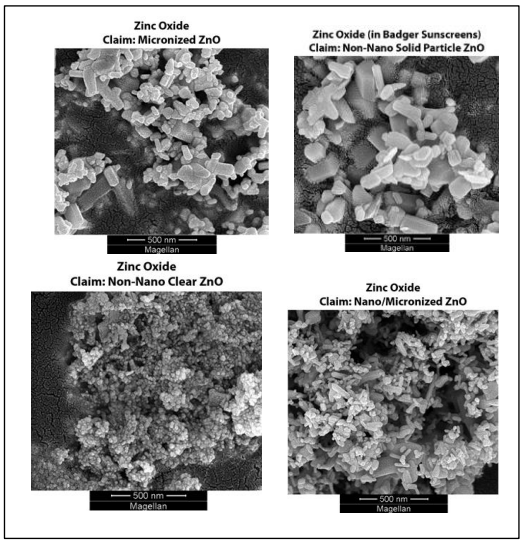

Fig. 2. Scanning Electron Microscope Images of Four Sunscreen Zinc Oxides.

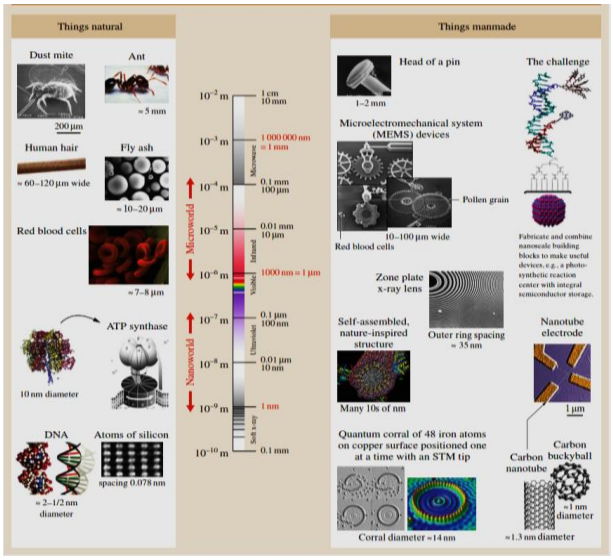

Fig. 3, The scale of things, nanometer and more (Vajtai, 2013).

https://www.badgerbalm.com/s-33-zinc-oxide-sunscreen-nanoparticles.aspx

Nanoparticles are particles between 1 and 100 nanometers in size which behave as a whole unit with respect to its transport and properties[3]. In Fig. 3, a comparative scale is displayed to demonstrate object with sizes.

Recently scientists have begun to focus on optical properties of metallic colloids since the early twentieth century with Gustav Mie's works (Hashim, 2012). However, the use of nanoscale material and particularly metal oxide is much older and trace back to several millennia ago (Colomban, 2009). For examples some natural clays used in antique potters were Nano-sized or Chines are famous to use Au nanoparticles to introduce red color in their ceramic porcelains more than thousand years ago (Cao, 2004). Also the invention and use of Ceramic Matrix Composites (CMCs) made from natural nanosized dates back to the Iron Age. This kind of material is the mixture of asbestos, a rock yarn made of ~10nm and clays which were used as utensils for cooking (Colomban, 2009).

In nanotechnology because the greater fraction of atoms gather at the surface so it and its properties become extremely important (Carter & Norton, 2007). The shape and size of this atoms determine the physical, chemical and optical properties of the surface (Vajtai, 2013), (Roqué, Molera, Sciau, Pantos, & Vendrell-Saz, 2006). The aforementioned fact can obviously be detected in the Medieval lustre pottery, Lycurgus cup and Roman red tesserae and etc. which owe their special properties to nanoparticle of copper and other noble metal oxide in their compositions (Brun, Mazerolles, & Pernot, 1991), (Cao, 2004), (Carter & Norton, 2007).

The purpose of this paper is to present a review on the use of metal nanoparticles by potters to give the recent state of the art and technology.

Samples Of Glass and Ceramics Containing Nanoparticles

Investigations using various techniques showed that the source of red color in glasses of the late Bronze Age (1200-1000 BCE) from Frattesina di Rovigo (Italy) was copper nanoparticles (Angelini et al., 2004). Beside the glasses, the presence of copper nanoparticles and cuprite (Cu_2O) had been reported in the Celtic red enamels dated from 400 to 100 BC (Fig. 4) (Brun et al., 1991).

[3] . Module 3: Characteristics of Particles – Particle Size Categories

Fig.4, Enamel on the escutcheon from Hitchin, Hertfordshire (Bruce-Mitford & Raven, 2005).

The usage of metallic particles like copper for coloring glass spread during the Roman period (Brun et al., 1991). It is reported that the huge number of mosaic tesserae produced during Roman period contain copper nanoparticles (Fig.5) (Wilson, 2013), (Arletti, Quartieri, & Vezzalini, 2006), (Colomban, 2009). It is known that Byzantine mosaic tesserae were the most expensive and elaborated mural decorations (James, 2006), (Shugar, 2000).

Fig.5, Mosaic of OT kings, tesserae mosaic sample, San Marco Museum, Venice.

Chemical analysis (Table 1) and XRPD pattern of some tesserae mosaic found in Pompeii excavation indicated the presence of cuprite (Cu_2O) and malachite ($Cu_2CO_3(OH)_2$) with particles smaller than 1μm in the samples.

Table 1, chemical analysis of red tesserae sample found in Pompeii.

Al2O3	TiO_2	MnO	MgO	FeO	CaO	Na_2O
1.57	0.26	0.01	0.47	0.64	3.03	14.33
K_2O	P_2O_5	Sb_2O_5	Cu_2O	PbO	CoO	SiO_2
0.22	0.02	1.45	8.40	23.88	0.39	46.35

Large dendritic crystals of cuprite and malachite element responsible for the red opaque color in the mentioned tesserae fragments (Fig. 6) (Arletti et al., 2006).

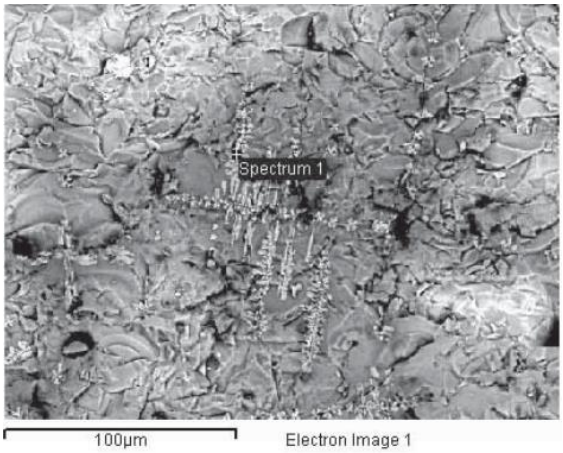

Fig.6, BSE image of red tesserae sample, showing the presence of dendrite of cuprite.

In addition to the copper, gold and silver nanoparticles have been utilized to create color in the glass for thousands of years. The most precious samples are universally famous Lycurgus cup and small and large stained glass for castles and cathedrals (Fig. 7). Lycurgus cup made by Romans in the 4th century and includes gold and silver nanoparticles. The reported Chemical analysis of the glass of cup by Chirnside and Profitt (1963 and 1965) is given in the (Table 2).

Table 2. The composition of the Lycurgus Cup based on the data of the Brill (1965) (Barber & Freestone, 1990).

SiO_2 73,5	MgO 0,5 – 0,6	P_2O_3 0,2	SnO_2 < 0,01	
Na_2O 13 – 15	Al_2O_3 2,5	Sb_2O_5 0,3	B_2O_3 0,1	
CaO 6,5	Fe_2O_3 1,5	CuO 0,04	TiO_2 0,07	
K_2O 0,9	MnO 0,45	PbO 0,2	Ag 0,03	Au 0,004

The optical properties of this cup were caused by the presence of a fine particle of gold and probably alloyed with silver. This cup is noted for the unusual optical effect by changing light source. It appears green in reflected light (if the light source is outside) and appears red in transmitted light (if the light source is within the cup) (Vajtai, 2013). It has been demonstrated that spectacular color change caused by colloidal metal and more precisely by

nanocrystals of a silver-gold alloy dispersed through the glassy matrix. The gold particles are mainly responsible for the reddish transmission and the silver for the greenish reflection (Barber & Freestone, 1990).

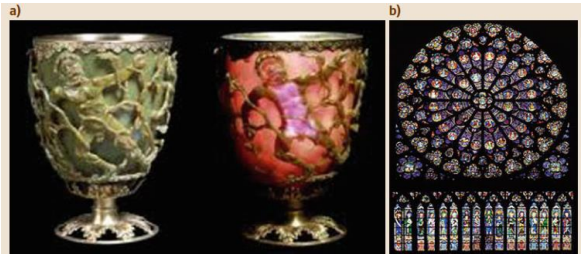

Fig.7, **a**), Lycurgus cup in reflected and transmitted light. **b**), The south rose window of Notre Dame Cathedral in Paris, France (Vajtai, 2013).

During the Middle Age glass manufacturing expanded substantially and it was accompanied by an increase in the type of colloidal metals for coloring glass (Kurmann-Schwarz & Lautier, 2009), (Pérez-Villar, Rubio, & Oteo, 2008). This age is also coincident with the producing lustre ware, a special type of glazed ceramic with attractive optical effects again caused by metallic nanoparticle (Caiger-Smith, 1985), (Hashim, 2012), (Carter & Norton, 2007), (NayebPashaee, Aarabi, Sarpoolaky, & Vafaeenezhad, 2015).

Luster is a variety of decorative metallic thin film about 200nm- 500nm thick that was applied on the surface of Medieval glazed ceramics (Pérez-Arantegui et al., 2001), (Carter & Norton, 2007). The first examples were produced at the court of the Abbasid in the Baghdad and Fatimides honed this technique to perfection and then introduced to the Islamic world (Boch & Niepce, 2010), (Colomban, 2009), (Sciau, 2012). In the (1237-1492 CE) luster decorating technique has thrived in Spain andfound a new application in the lustered glazed majolica during Italian Renaissance. The main luster production centers are summarized in (Fig.8)

Fig.8, localization of the main centers of luster productions.

Fig .9 shows a sample of this kind of decoration and the TEM analysis indicate the presence of copper nanoparticles in the luster glaze.

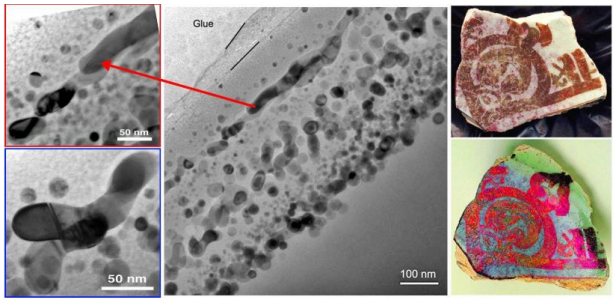

Fig.9, Lustre from the Fatimid period (12th century CE) showing a partial multi-layer silver nanoparticle organization. On the right, the colour change from brown (scattering light) to pink (specular position) and on the left, magnifications of elongated silver particles ("metal worms")(Mirguet, Roucau, & Sciau, 2009), (Chabanne, Bouquillon, Aucouturier, Dectot, & Padeletti, 2008).

The technique of heating glass, coated with silver-based is assigned to Coptic glassmaker in Egypt/ Syria has been in the sixth or seventh century that according to the reports its color change with the observation angle. It is consistent with the production of luster glass before Islamic Times. But this kind of decorated glass was not as shine as luster pottery (Colomban, 2009). In the Fig. 10 some examples of luster decorated glass are given below.

Fig.10, Examples of luster Fatimid glasses. (Colomban, 2009)

Nanoparticles have been recently developed for new method decoration technique onto the ceramics. A novel field of application is decorated by ink-jet printing. The nanoscale materials are able to overcome the problems caused by micronized pigments such as low coloring performance, nozzle closing or dispersion instability (Gardini et al., 2008). Additionally, tribological and mechanical properties of the surface such as scratch, abrasion resistance, and hardness can be developed by using

nanoparticles (Perera, 2004). Also, the nanoparticles are smaller than the wavelength of the visible spectrum. It means that there is no scattering and reflecting accrue in the visible light, therefore, produced material is transparent (Cavalcante, Dondi, Guarini, Raimondo, & Baldi, 2009).

Nowadays besides the artistic and decorative usage of a nanosized particle in the ceramic and glass, the most important and common application field of nanomaterials are bioceramics and nanocomposites (Hench, 1991), (Hench & Wilson, 1993). Fig. 11 shows the application of bioceramics for repairing the decayed tooth.

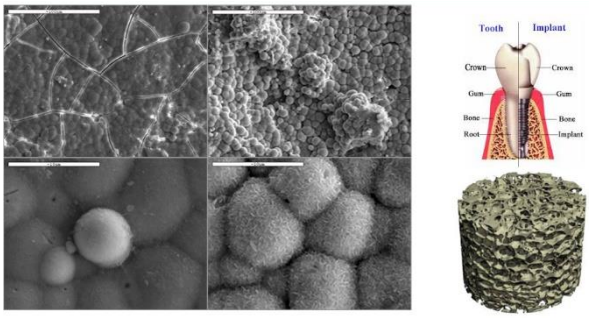

Fig. 11, Ceramic biomaterials for dental application.
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Conclusion

Different analysis on the ancient glass and ceramics revealed the presence of nanoparticles in the composition of the materials. Since the ancient potters and glassmakers did not have any nanostructure checking facilities and were not aware of material structure, these analyses show the high-level empirical control carried out by potters and glassmakers. Ceramic and glass found in the excavations show the presence of nanoparticles in the base of the samples. Distribution of these materials allowing for the obtainment of very high iridescent color, resistance against acidic and alkaline chemicals and having a transparent view. Nowadays besides the mentioned application of nanoparticles in the glass and ceramics, nanosized materials have got widespread usage in the ceramic composites and bioceramics.

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