Nanoparticles in Ancient Materials: The Metallic Lustre Decorations of Medieval Ceramics

Philippe Sciau CEMES-CNRS, Université de Toulouse France

1. Introduction

The scientific community has begun to focus on optical properties of metallic colloids since the early twentieth century with Gustav Mie's works (Mie 1908). However the use of their outstanding properties is much older and dates back to several millennia ago (Colomban 2009; Garcia 2011).

Investigations using various techniques showed that red glasses of the late Bronze Age (1200-1000 BCE) from Frattesina di Rovigo (Italy) were coloured thanks to the excitation of phasmon surface modes of copper nanoparticles (Angelini et al. 2004; Artioli et al. 2008). The protohistoric community of this region developed advanced glass-manufacturing technology and was able to induce the exsolution of metallic copper crystals in the top layer of glass by exposing the material to reducing conditions. The presence of copper nanoparticles and cuprous oxide (cuprite Cu₂O) had already been reported in Celtic red enamels dated from 400 to 100 BCE (Brun et al. 1991). The use of metallic particles for colouring glass spread during the Roman period. Most of the red tesserae used in Roman mosaics were made of glass containing a dispersion of copper nanocrystals (Brun, Mazerolles et al. 1991; Colomban et al. 2003; Ricciardi et al. 2009). In addition to the copper crystals, gold nanoparticles were identified in some red tesserae showing that other metallic nanocrystals were used during Roman times (Colomban, March et al. 2003). It is precisely the case of the well-known Roman Lycurgus Cup in glass dated from the 4th century CE and currently exhibited in the British Museum (Freestone et al. 2007). The glass of this cup is dichroic and resembles jade with an opaque greenish-yellow tone, but when light shines through the glass (transmitted light) it turns into a translucent ruby colour. It has been demonstrated that the spectacular colour change is caused by colloidal metal and more precisely by nanocrystals of a silver-gold alloy dispersed throughout the glassy matrix (Barber & Freestone 1990). A handful of other Roman glasses showing a dichroic effect were also reported and although the colour change is not so spectacular, the Lycurgus Cup is obviously the result of a good technical mastery of Roman glass-workers (Freestone, Meeks et al. 2007). The Roman craftsmen knew that glass could be red coloured and that unusual colour change effect generated by the addition of noble metal bearing material when the glass was molten could be engineered. Nevertheless, the difficulties in controlling the coloration process meant that relatively few glasses of this type were produced, and even fewer have survived.

During the Middle Ages, glass manufacturing expanded considerably, especially to address the demand for stained glass (Kurmann-Schwarz & Lautier 2009). This development was accompanied by an increase in the type of colloidal metal used for colouring glass (Perez-Villar *et al.* 2008; Rubio *et al.* 2009; Gimeno *et al.* 2010). This age also saw the emergence of lusterware, a special type of glazed ceramics, with striking optical effects again obtained from metallic nanoparticles (Caiger-Smith 1991; Pérez-Arantegui *et al.* 2001). Then the progress in glass chemistry during the Renaissance period (Simmons & Mysak 2010) and especially in modern times allowed for better tuning of coloration effects based on the surface plasmons of metallic nanoparticles (Gil *et al.* 2006; Hartland 2011).

The manufacturing process of red glass was used worldwide. The famous Satsuma glasses produced in Japan in the mid-19th century were obtained using a similar technique and their ruby colour comes also from the absorption properties of copper nanocrystals (Nakai *et al.* 1999). It is also the case of the famed red *flambé* and mixed blue-red Jun glazed porcelains from Song and Ming to Qing Chinese Dynasties (Wood 1999).

2. Lustre decorations of medieval ceramics

The lustre is a variety of glaze decoration on ceramics, which appears in medieval times as mentioned in the introduction. Like the ruby glass, the colour of the lustre decorations has a physical basis coming from metallic nanoparticles (Bobin et al. 2003; Colomban 2009; Lafait et al. 2009). However, lustres possess the particularity of having a colour which can change depending on the angle from which it is observed. An example of these types of ceramic decorations is given in Figure 1 (Mirguet, Roucau et al. 2009). The colour change under specular reflection is often spectacular and produces a very intense coloured metallic shine, which can be golden-yellow, blue, green, pink, etc ... The density of nanoparticles in the top layers of glaze is higher than that for ruby glass and shows a structuration in depth, which can be more or less complex, as in the lustre of figure 1. This multi-layer structuration on the scale of wavelengths of visible light gives rise to interference phenomena and scattering through rough interfaces, which adds to the surface plasmon effect and strongly contributes to the observed colour. As pointed out by Jacques Lafait et al. in their paper concerning the physical colours in cultural heritage, the colours with structural origin are particularly striking and very brilliant. The understanding of these structural effects on optical properties (photonic crystals) is very recent and it is fascinating to see that Islamic potters were able to create such complex structure through empirical chemical means in order to exploit their outstanding optical properties. However before going into detail about these various aspects, a word about the historical context in order to have a few chronological and geographic references.

2.1 Historical context

The earliest lustred potteries were found in Mesopotamia and most of them originate from the site of the Abbasid Caliphs' palace of Samarra in present-day Iraq (Caiger-Smith 1991). This monumental palace-complex whose building was begun by Caliph Mu'tasim in 836 CE, was abandoned in 883 CE.

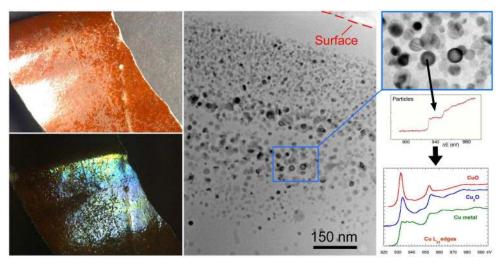


Fig. 1. 9th century CE lusterware from Mesopotamia (Susa). The colour changes from red (top left) to blue/green (bottom left) (Micrographs, courtesy D. Chabanne), nanoparticle distribution observed by TEM (in the centre) and on the right, the identification of particle nature (copper metal) by EELS. Details can be found in references (Chabanne 2005) and (Mirguet *et al.* 2009).

The early lustre manufacturing is therefore rather well dated, though it is currently assumed that first experiments may have occurred earlier, possibly in the time of Harun-al-Rashid (766-809 CE). Abbasid lustres were also found in some quantity in other Mesopotamian cities such as Baghdad, Basra, Kufa or Susa in present-day Iran. Theses cities are often presented as potential production centres, but it is yet an open question. Mesopotamian lustres were discovered outside this geographic area. Tiles with lustre decorations from Iraq were used in the partial reconstruction of the Kairouan Great Mosque (Tunisia), in the 9th century. Fragments have been found at Fustat, which was the main citadel of Lower Egypt in the 9th century. Shards have also been excavated from the site of the palace of Qal'a in Algeria, which was until 1052 CE the capital of the Hammamid princes. In fact, lustre decorations were certainly created in the early 9th century for courts and courtiers and seldom appeared in any other setting. For several centuries the lusterware kept its status of luxury tableware for princely courts.

The annexation of Egypt by the Fatimids (969 CE) led to profound modifications, not only on a governmental level, but also in the population. The Fatimid capital was transferred from Tunisia to al-Qahira, modern Cairo, and the old city of Fustat provided quarters for craftsman who worked for the new capital a few kilometres to the north. The demand for lustre by the new court led to the development of the local production. It is now attested that lustres were made in Fustat before the Fatimid period. However this production, often called pre-Fatimid, seems to have been very limited and of poor quality. The Egyptian production actually began with the arrival of the Fatimids, and during two centuries, a great deal of good quality lustre was being made reflecting the interests and cultural traditions of the new dynasty and its courtiers.

During the 12th century, lustre technique began to extend from Egypt to Syria and to Persia (present-day Iran). Craftsmen from Fustat allegedly brought the technique there during the decline of the Fatimid dynasty, which occurred in the middle 12th century. Concerning the diffusion in Persia, the subject is treated in detail in Oliver Watson's book (Watson 1985).

It seems that the technique appeared in the Occident (southern Spain) during the same period, as soon as the taifa emerged after the dissolution of the Spanish Umayyad caliphate. However, it is only under the Nasrid dynasty (1237-1492 CE) that the lustre technique really flourished in Spain. Its apogee, between the 14th–15th centuries, gave rise to the Hispano-Moorish ceramic, which was elaborated in the Valencia region up to the 18th century.

The technique found a new application during the Italian Renaissance (15th and 16th centuries) where Deruta and Gubbio became the most famous production centres of lustred glazed majolica (Padeletti *et al.* 2006). The main production centres with chronological data are summarized in the figure 2.



Fig. 2. Localization of the main centres of lustre productions.

2.2 Nanoparticle layer

Many studies were devoted to determining the elementary composition of glazes. The results obtained by the C2RMF lustre team, which analysed a significant corpus of specimens, are available online¹. A review of the main results of the other studies can be found in Philippe Colomban's paper (Colomban 2009). The composition of glaze used in the lustre decoration is highly varied with alkaline and high lead glaze. There is not a specific composition. During the Abbasid times, the first productions used alkaline glazes but lead was then introduced with, in some cases, tin. The glazes used during the Fatimid epoch were mostly leaded alkaline. The Hispano-Moorish productions were characterized by high lead glaze containing a small amount of sodium and potassium. Renaissance decorations were also applied on leaded glazes. Significant composition variations were observed inside the same geographic area, which could be linked to a relative chronology, according to C2RMF's work. Several research groups are seeking to confirm this. The ceramic bodies are

¹Ceramics with metallic lustre decoration. A detailed knowledge of Islamic productions from 9th century until Renaissance. D. Chabanne, M. Aucouturier, A. Bouquillon1, E. Darque-Ceretti, S. Makariou, X. Dectot, A. Faÿ-Hallé, D. Miroudot (2011), 2011arXiv1101.2321C

also various. Some lustre decorations were affixed on ceramic clay bodies, whereas others were deposited on siliceous pasta. The various associations of ceramic/glaze in relation to the different geographic areas and periods are listed in the online paper of the C2RMF lustre team (cf. note 1).

The composition of nanoparticles is much less diverse. Only copper and silver were used in all lustre decoration from the 9th century to now. On the other hand, the size, the shape and the spatial organisation can be very different (Fig. 3). One of the best tools for studying an organisation on a nanometre scale is the transmission electron microscopy (TEM). It is this technique which allowed for the first observation of nanocrystals in an archaeological lustre, a 13th century lustre of Hispano-Moorish period (Pérez-Arantegui, Molera *et al.* 2001). Although it is an abrasive technique, which is an obstacle for the investigation of museum pieces, several specimens from different periods and different geographic areas have been analysed by TEM (Borgia *et al.* 2002; Padeletti & Fermo 2003b; Pérez-Arantegui & Larrea 2003; Fredrickx *et al.* 2004; Padeletti & Fermo 2004; Roqué *et al.* 2007; Mirguet *et al.* 2008; Mirguet, Roucau *et al.* 2009; Sciau *et al.* 2009a). For some of them, sampling was limited to a few thousand cubic micrometres, using focused ion beam (FIB) techniques (Sciau *et al.* 2009b). However, since these ceramics are not conductors, a carbon deposit must be performed, which is not easy to carry out on museum pieces.

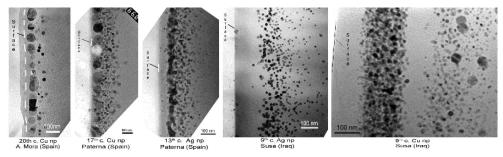


Fig. 3. A selection of bright field TEM images of various lustres from Mesopotamia (right) to Spain (left). More details can be found in the references (Chabanne 2005) and (Mirguet, Roucau *et al.* 2009).

Synchrotron radiation was used to obtain information on nanoparticles. In addition to the nature of nanoparticles, X-ray absorption fine structure (XAFS) measurements give interesting information on the presence of metallic ions (Ag+, Cu+, Cu²+) in the glassy matrix (Padovani *et al.* 2006). In some cases, the size of the metallic oxide clusters can be estimated by fitting the extended X-ray absorption fine structure (EXAFS) spectra, whereas the average size of metallic nanoparticles can be deduced from the broadness of X-ray diffraction reflections. In addition, using glancing incidence X-ray diffraction (GIXRD) techniques, information can be obtained on structure and depth distribution of nanoparticles (Bontempi *et al.* 2006). Nevertheless, all these techniques give only partial information about the nanoparticle layers and require a synchrotron facility.

An alternative solution has been proposed using ion beam analysis (IBA) (Salomon *et al.* 2008; Pichon *et al.* 2010). The association of particle induced X-ray emission (PIXE) and elastic Rutherford backscattering spectrometry (RBS) allowed them to obtain significant data

concerning the glassy matrix composition and the nature and the depth distribution of nanoparticles for a number of lustre ceramics, including valuable museum objects (Darque-Ceretti *et al.* 2005; Padeletti, Ingo *et al.* 2006; Chabanne *et al.* 2008; del Rio & Castaing 2010; del Rio *et al.* 2010). Whereas PIXE gives the chemical composition of the glassy matrix, RBS can provide detailed depth information. Thus, from a simulation of the experimental RBS spectrum, the nanoparticle distribution can be modelled. However, a calibration is necessary and for this, TEM observations are very useful (Chabanne, Bouquillon *et al.* 2008).

Several deductions can be made from all these investigations. The Abbasid and Fatimid samples observed by TEM showed a more complex structuration in depth than the Hispano-Moorish productions (Fig. 3). The particles of the first lustres are small with an average size of around 10-15 nm, and the thickness of the layer without particles below the glaze surface is superior to 100 nm (Chabanne 2005; Mirguet, Fredrickx *et al.* 2008). On the contrary, the Hispanic productions are characterized by a layer of big particles (50-100 nm) close to the glaze surface (Chabanne 2005; Mirguet, Roucau *et al.* 2009). This is even more pronounced for the 17th century lustres and modern replica made by Spanish artisans using a traditional process. Several Abbasid and Fatimid lustres present a partial structuring in depth such as shown in figure 3 and 4.

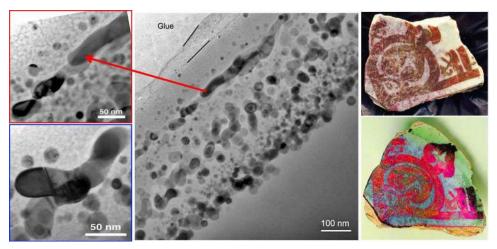


Fig. 4. Lustre from the Fatimid period (12th century CE) showing a partial multi layer silver nanoparticle organization (Mirguet, Roucau *et al.* 2009; Sciau, Mirguet *et al.* 2009a). On the right, the colour change from brown (scattering light) to pink (specular position) and on the left, magnifications of elongated silver particles ("metal worms").

TEM investigations even brought to light a lustre decoration from the Fatimid period with a very regular nanoparticle distribution in two well-separated layers (Fig. 5). Electron diffraction revealed that all particles were silver with a CFC structure (Sciau, Mirguet *et al.* 2009a). The electron energy loss spectroscopy (EELS) confirmed that silver is only present in the nanoparticle layers whereas copper is found everywhere in the glaze, however in the ionic form (Cu²⁺). The green colour of the glaze indeed comes from the Cu²⁺ ions. The distance between the two layers is amazingly constant. With a value of around 430 nm, this distance is of the same order of magnitude as visible wavelengths. It results in that this

double layer structure behaves as an optical network. A more in depth investigation of nanopaticles showed that the particles in the second layer are slightly larger and that their shapes are less spherical. Some particles have even coalesced forming larger particles. High resolution electron microscopy (HREM) showed that many of them have structural defects of a stacking fault type (Sciau, Mirguet *et al.* 2009a).

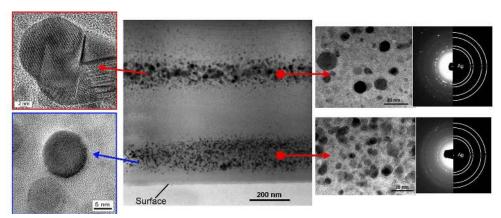


Fig. 5. Lustre from the Fatimid period (12th century CE) showing a well defined multi layer silver nanoparticle organization, with on the left, HREM images of nanoparticles of each layer and on the right, electron diffraction identification (Mirguet, Roucau *et al.* 2009; Sciau, Mirguet *et al.* 2009a).

2.3 Optical properties

Since the discovery of their astonishing colorimetric properties, several studies have sought to model the optical behaviour of lustre decorations.

Olivier Bobin was the first to carry out a theoretical investigation of optical properties of lusterware and thus to prove the role of the surface phasmon resonance of silver and/or copper nanocrystals in the colouring process (Bobin, Schvoerer et al. 2003). His modelling, using Mie's theory, and based on the copper-silver ratio, the particle size, the particle density and the nature of embedded glaze give rather good results for the colours observed in scattering light. In the modelling of the size effect on the surface plasmon resonance, two regimes are usually distinguished depending on the nanoparticle size range (Garcia 2011). For the small particles (smaller than light wavelength i.e. with a radius up to 50 nm), the particle can be properly described by a dielectric dipole. The size variation affects mainly the width and the intensity of the resonance band. On the other hand, the resonance wavelength is only slightly shifted. For the larger particles with a size comparable to the wavelength i.e. with a radius superior or equal to 50 nm, the dipole approximation is not sufficient and multipolar terms must be added leading to the splitting of the resonance band into several peaks: two peaks for quadrupole, three peaks for an octopole, etc ... (Kreibig et al. 1987). The metallic particles present in the lusterware are seldom superior to 50 nm in radius (cf. § 2.2); also the dipole approximation is sufficient to describe the surface plasmon resonance. Nevertheless, the size dispersion is large and that has as a consequence a significant broadening of the absorption band. Since the restoring force for surface plasmons

is related to the charge accumulated at the surface, it is influenced as well by the particle shape. With elongated particles, the absorption band is split into two bands: the transversal and longitudinal bands. The frequency shift is proportional to the ratio between longitudinal and transversal lengths. While the resonant frequency of transversal plasmons falls at about the same position as for spherical particles (actually, at wavelengths slightly smaller), the resonance of longitudinal plasmons shifts towards larger wavelengths when the ratio increases. The intensity of the longitudinal plasmon band increases with the ratio while the one of the transversal band decreases. For the lustre of figure 4, the shape effect must be taken into account, but in this case other effects such as the interference phenomena must also be considered. It is obvious that the interferences have a significant influence on the colour of metallic shine (the specular position) for the lustres having a partial multi-layer structuration. The study of the lusterware with the double layer (Fig. 5) demonstrated that the interferences are at the origin of the colour variation of the metallic shine from blue to green (Sciau, Mirguet *et al.* 2009a).

The first model taking into account the interference phenomena was proposed by Vincent Reillon (Reillon & Berthier 2006). However, the modelling of such a complex system was not easy and it was only recently that a model integrating all phenomena (surface plasmon absorption, interference and scattering) was published (Reillon 2008; Reillon *et al.* 2010). From this model, it is now possible to correctly simulate the reflection spectra recorded as well in the specular direction as in the scattering directions. The evolution of the colour between the specular and the diffusion directions can be perfectly calculated. Thus, the key parameters determining colour behaviour are (Lafait, Berthier *et al.* 2009):

- in the specular direction, interference phenomena play a major role with the key parameters being the number of layers, the optical index and the thickness of each layer,
- in the scattering cone, plasmon absorption is predominant and the key parameters are
 the kind of metal, the metal volume fraction, the particle size and shape, and the glass
 matrix composition,
- in the intermediate cone, there is a transition between a coherent component (dominant close to the specular direction) and a scattered incoherent component (dominant close to the scattering cone).

The colour behaviour of lustre is schematized in figure 6. To simulate the experimental spectra, the modelling uses a schematic representation of the multilayer structure of lustre decoration. Hence inversely from a modelling of a set of experimental spectra collected from different directions, it is possible to obtain significant information on the nanoparticle distribution.

2.4 Manufacturing process

Several descriptions of the glazing technique were proposed (Pérez-Arantegui, Molera et al. 2001; Padeletti & Fermo 2003a; Colomban & Truong 2004; Pradell et al. 2005; Roqué et al. 2005; Pradell et al. 2006; Roqué et al. 2008; Colomban 2009) on the basis of experimental evidence and on information extracted from the transcription of ancient recipes (Abu al Qâsem 14th century, Picolpasso 16th century, Deck and Bertan 19th century and Artigas 20th century).

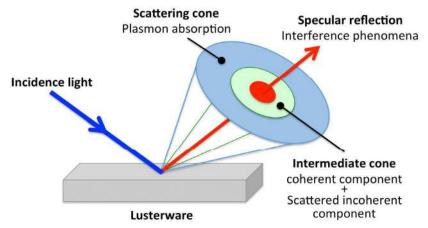


Fig. 6. Schematic representation of the light scattered and reflected by a lustre glaze decoration from Reillon's modelling (Reillon 2008; Reillon, Berthier *et al.* 2010).

Lustre decorations were obtained by applying a mixture of a paint, which contained copper and silver salts, water and more or less vinegar and lye, onto a glazed ceramic, which was subsequently annealed in a reducing atmosphere. Inside the kiln, the raw paint reacted with the glaze surface, and after firing, the remaining paint was washed off, revealing the lustre decoration beneath.

The role of ionic exchange was first identified in the lustre formation process (Smith et al. 2003; Pradell, Molera et al. 2005). From the analysis of medieval ceramics, some interesting trends and information were obtained concerning the driving force responsible for the diffusion of silver and copper ions into the glaze, consisting of an "ionic exchange" of Ag+ and Cu+ with Na+ and K+. This type of ionic exchange is a well-known mechanism in glasses and glazes (Pradell, Molera et al. 2006). When glasses are immersed in a solution containing copper and/or silver molten salt (typically sulphates or nitrates), atomic exchanges take place and the alkalis (K+ and Na+) of the glaze are replaced by Ag+ and Cu+ ions of the solution. Accurate chemical analysis of medieval ceramics showed a clear inverse correlation between the metal components of the lustre decorations (Cu and Ag) and the amount of Na and K in the glaze. This correlation has been found in early Islamic lusterwares from Iraq (9th century CE) as well as in late Hispano-Moorish lusterwares from Paterna (13th-17th centuries CE). In addition, reproductions and ancient lustre surfaces were observed by means of white light interferometry, atomic forces microscopy, X-ray diffraction and electron microprobe (Roqué, Pradell et al. 2005). These observations showed that lustre layers do not appear as superimposed layers on the top of the glaze, but rather as a surface roughness resulting in the nanocrystals growth inside the glassy matrix. The surface roughness increases during the formation process as a result of metal nanoparticle growth. The lustre formation process involves a two step process: ion exchange and crystallization (nucleation and crystal growth) of copper and silver metallic nanoparticles inside the glassy matrix (Roqué, Molera et al. 2008).

More recently, it has been assumed that the burning of organic residues could be used to control the surface temperature and embedded metal dispersion allowing one to set the final lustre colour in different places of the same item (Mirguet, Fredrickx et al. 2008). The strong temperature gradient arising from the combustion of surface acetate residues could control the self-organization of the metal particles leading to light diffraction. The multilayer particle distribution of lustre could be explained by special firing cycles where repeated heat flashes provoked by surface organic residue combustion make it possible to control the size, the shape and the distribution of nanoparticles. In several cases, very elongated silver particles ("metal worms") were observed by TEM. It is particularly well marked in the Fatimid lustre of Figure 4, which shows 3 layers of metal worm particles separated by areas of lower density in nanoparticles. The particles of these intermediate zones are smaller and spherical. The nanoparticle coalescences forming larger particles are also observed in the second layer of the double layer lustre (Fig. 5). High-resolution electron microscopy (HREM) showed that many of them have structural defects of a stacking fault type. It is not the case of nanoparticles of the first layer, which are smaller and quite spherical. The nanoparticles of the two layers are different enough to conclude that they were not formed under the same thermal conditions. Nanoparticle coalescences were also found in the two other lustres of figure 3 with silver particles (Abbasid from Susa and 13th century from Paterna).

The elongated shape of silver particles proves that the temperatures close to that of the silver melting point (\sim 960°C) were reached. Diffusion-controlled phenomena cannot lead to such worm-shapes. The Melting of metallic silver demonstrates that glaze surface temperatures close to 1000°C were achieved at the peak temperature cycle. This is consistent with an increase in temperature obtained thanks to the combustion of organic residue. Except for some modern replica (Mora productions, Fig. 3), worm-shapes were not observed for copper particles, which indicated that the melting point of copper (\sim 1080°C) was not reached.

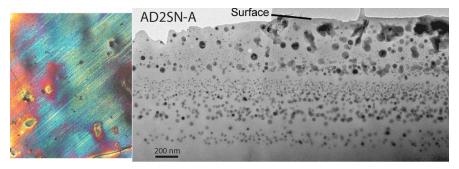


Fig. 7. Lustre creation made by Eva Haudum (Colomban 2009).

3. Conclusion

The review of present knowledge on ancient materials, in which the size and distribution as well as the reduction of metallic nanoprecipitates were organized, shows the high level of empirical control carried out by ancient potters and glass-makers. The ancient potters were certainly not aware of material nanostructuration, since they did not have any nanostructure checking facilities. However, their know-how allowed for the realization of two perfectly well separated layers (Sciau, Mirguet *et al.* 2009a). This special

nanostructuration has been up to now observed on only one sample. It is important to keep in mind that this sample might have been accidently obtained or that the first layer (uppermost one) was created because the first visual aspect did not suit the craftsman. However, other lustres of the Fatimid (12th century CE) and Abbasid (9th - 10th centuries CE) periods show a partial organisation in multi-layered nanoparticles. So there is a good chance that this sample is not an isolated case and that this technology was developed by the Islamic craftsmen to exploit the complex nano-optical properties of multi layered particles.

The optical modelling performed by Vincent Reillon confirmed the role of interference in the colour of metallic shine reflection (specular direction). It is obvious that the multi-layer organisation of nanoparticles, with distances between layers comparable to the visible wavelengths, strengthens the interference effects allowing for the obtainment of very bright iridescent colours from a large palette of hues. It is likely that it was the aim of the Abbasid and Fatimid potters to develop empirical processes for creating such multi-layered nanoparticles through a know-how, which has nowadays partially been lost. Modern artists (S. Çizer, E. Haudum ...) search to recreate lustre decorations with strong iridescent effects and bright colours using modern kilns permitting alternative oxidising (oxygen flux) and reducing (CO flux) phases during the firing (Colomban 2009). Their best recreations exhibit the partial multi-layer structure observed in the Abbasid and Fatimid artefacts, but maybe with a weaker organisation and sometimes residues of raw mixture as observed in figure 7.

4. Acknowledgments

I would like to thank A. Bouquillon and D. de Camaret for their help in the writing of this chapter as well as colleagues who allowed me to develop this activity in CEMES-CNRS lab (G. BenAssayag, B. Brunetti, R. Carles, Ph. Colomban, H. Dexpert, C. Roucau). I thank all under-graduate and PhD students who experimentally contributed to this paper, especially D. Chabanne, C. Dejoie, Y. Leon, C. Mirguet and J. Roqué-Rosell. Research supported by the *Conseil Régional de Midi-Pyrénées* under several contracts.

5. References

- Angelini, I.; Artioli, G.; Bellintani, P.; Diella, V.; Gemmi, M.; Polla, A. & Rossi, A. (2004). Chemical analyses of bronze age glasses from Frattesina di Rovigo, northern Italy. *Journal of Archaeological Science*, Vol.31, No.8, pp. 1175-1184, ISSN 0305-4403
- Artioli, G.; Angelini, I. & Polla, A. (2008). Crystals and phase transitions in protohistoric glass materials. *Phase Transitions*, Vol.81, No.2-3, pp. 233-252, ISSN 0141-1594
- Barber, D. J. & Freestone, I. C. (1990). An investigation of the origin of the color of Lycurgus cup by analytical transmission electron-microscopy. *Archaeometry*, Vol.32, (February 1990), pp. 33-45, ISSN 0003-813X
- Bobin, O.; Schvoerer, M.; Miane, J. L. & Fabre, J. F. (2003). Coloured metallic shine associated to lustre decoration of glazed ceramics: a theoretical analysis of the optical properties. *Journal of Non-Crystalline Solids*, Vol.332, No.1-3, (December 2003), pp. 28-34, ISSN 0022-3093

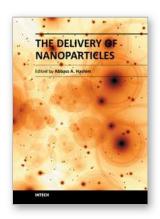
- Bontempi, E.; Colombi, P.; Depero, L. E.; Cartechini, L.; Brunetti, B. G. & Sgamellotti, A. (2006). Glancing-incidence X-ray diffraction of Ag nanoparticles in gold lustre decoration of Italian Renaissance pottery. *Applied Physics A: Materials Science & Processing*, Vol.83, No.4, (Jun 2006), pp. 543-546, ISSN 0947-8396
- Borgia, I.; Brunetti, B.; Mariani, I.; Sgamellotti, A.; Cariati, F.; Fermo, P.; Mellini, M.; Viti, C. & Padeletti, G. (2002). Heterogeneous distribution of metal nanocrystals in glazes of historical pottery. *Applied Surface Science*, Vol.185, No.3-4, (January 2002), pp. 206-216, ISSN 0169-4332
- Brun, N.; Mazerolles, L. & Pernot, M. (1991). Microstructure of opaque red glass containing copper. *Journal of Materials Science Letters*, Vol.10, No.23, (December 1991), pp. 1418-1420, ISSN 0261-8028
- Caiger-Smith, A. (1991). Lustre pottery. Technique, tradition and innovation in Islam and the Western World, New Amsterdam Books, ISBN 1-56131-030-1, New York, USA.
- Chabanne, D. (2005). Le décor de lustre métallique des céramiques glaçurées (IXème-XVIIème siècles). Matériaux, couleurs et techniques. PhD thesis, University Bordeaux 3.
- Chabanne, D.; Bouquillon, A.; Aucouturier, M.; Dectot, X. & Padeletti, G. (2008). Physicochemical analyses of Hipano-Moresque lustred ceramic: a precursor for Italian majolica? *Applied Physics A: Materials Science & Processing*, Vol.92, No.1, (July), pp. 11-18, ISSN 0947-8396
- Colomban, P. (2009). The use of metal nanoparticles to produce yellow, red and iridescent colour, from bronze age to present times in lustre pottery and glass: solid state chemistry, spectroscopy and nanostructure. *Journal of Nano Research*, Vol.8, pp. 109-132, ISSN 1662-5250
- Colomban, P.; March, G.; Mazerolles, L.; Karmous, T.; Ayed, N.; Ennabli, A. & Slim, H. (2003). Raman identification of materials used for jewellery and mosaics in Ifriqiya. *Journal of Raman Spectroscopy*, Vol.34, No.3, (March 2003), pp. 205-213, ISSN 0377-0486
- Colomban, P. & Truong, C. (2004). Non-destructive raman study of the glazing technique in lustre potteries and faience (9-14th centuries): silver ions, nanoclusters microstructure and processing. *Journal of Raman Spectroscopy*, Vol.35, No.3, (March 2004), pp. 195-207, ISSN 0377-0486
- Darque-Ceretti, E.; Hélary, D.; Bouquillon, A. & Aucouturier, M. (2005). Gold like lustre: nanometric surface treatment for decoration of glazed ceramics in ancient Islam, Moresque Spain and Renaissance Italy. *Surface Engineering*, Vol.31, No.5-6, (December 2003), pp. 352-358, ISSN 0267-0844
- del Rio, A. P. & Castaing, J. (2010). Lustre decorated ceramics from a 15th-16th century production in Seville. *Archaeometry*, Vol.52, (February 2010), pp. 83-98, ISSN 0003-813X
- del Rio, A. P.; Roehrs, S.; Aucouturier, M.; Castaing, J. & Bouquillon, A. (2010). Medinal Al-Zahra lustre ceramics: 10th century local nanotechnology or importation from middle east. *Arabian Journal for Science and Engineering*, Vol.35, No.1C, (Jun 2010), pp. 157-168, ISSN 1319-8025

- Fredrickx, P.; Hélary, D.; Schryvers, D. & Darque-Ceretti, E. (2004). A TEM study of nanoparticles in lustre glazes. *Applied Physics A: Materials Science & Processing*, Vol.79, No.2, (July 2004), pp. 283-288, ISSN 0947-8396
- Freestone, I.; Meeks, N.; Sax, M. & Higgitt, C. (2007). The Lycurgus Cup A Roman nanotechnology. *Gold Bulletin*, Vol.40, No.4, pp. 270-277, ISSN 0017-1557
- Garcia, M. A. (2011). Surface plasmons in metallic nanoparticles: fundamentals and applications. *Journal of Physics D: Applied Physics*, Vol.44, No.28, (July 2011), pp. 283001, ISSN 0022-3727
- Gil, C.; Villegas, M. A. & Navarro, J. M. F. (2006). TEM monitoring of silver nanoparticles formation on the surface of lead crystal glass. *Applied Surface Science*, Vol.253, No.4, (December 2006), pp. 1882-1888, ISSN 0169-4332
- Gimeno, D.; Aulinas, M.; Bazzocchi, F.; Fernandez-Turiel, J. L.; Garcia-Valles, M.; Novembre, D.; Basso, E.; Messiga, B.; Riccardi, M. P.; Tarozzi, C. & Mendera, M. (2010). Chemical characterization of the stained glass window from the rose window, Siena Duomo (Italy, 1288-1289). *Boletin De La Sociedad Espanola De Ceramica Y Vidrio*, Vol.49, No.3, (May-Jun 2010), pp. 205-213, ISSN 0366-3175
- Hartland, G. V. (2011). Optical Studies of Dynamics in Noble Metal Nanostructures. *Chemical Reviews*, Vol.111, No.6, (Jun 2011), pp. 3858-3887, ISSN 0009-2665
- Kreibig, U.; Schmitz, B. & Breuer, H. D. (1987). Separation of plasmon-polariton modes of small metal particles *Physical Review B*, Vol.36, No.9, (September 1987), pp. 5027-5030, ISSN 0163-1829
- Kurmann-Schwarz, B. & Lautier, C. (2009). The Medieval stained-glass window in Europe: 10 years of abundant research. *Perspective-La Revue De L Inha*, No.1, (March 2009), pp. 99-130, ISSN 1777-7852
- Lafait, J.; Berthier, S.; Andraud, C.; Reillon, V. & Boulenguez, J. (2009). Physical colors in cultural heritage: surface plasmons in glass. *Comptes Rendus Physique*, Vol.10, No.7, (September 2009), pp. 649-659, ISSN 1631-0705
- Mie, G. (1908). Beiträge zur optik trüber medien, speziell kolloidaler metallösungen. *Annalen der Physik*, Vol.25, No.3, (March 1908), pp. 377-445, ISSN 0003-3804
- Mirguet, C.; Fredrickx, P.; Sciau, P. & Colomban, P. (2008). Origin of the self-organisation of Cu°/Ag° nanoparticles in ancient lustre pottery. A TEM study. *Phase Transitions*, Vol.81, No.2-3, pp. 253-266, ISSN 0141-1594
- Mirguet, C.; Roucau, C. & Sciau, P. (2009). Transmission electron microscopy a powderful means to investigate the glazed coating of ancient ceramics. *Journal of Nano Research*, Vol.8, pp. 141-146, ISSN 1662-5250
- Nakai, I.; Numako, C.; Hosono, H. & Yamasaki, K. (1999). Origin of the red color of satsuma copper-ruby glass as determined by EXAFS and optical absorption spectroscopy. *Journal of the American Ceramic Society*, Vol.82, No.3, (March 1999), pp. 689-695, ISSN 0002-7820
- Padeletti, G. & Fermo, P. (2003a). How the masters in Umbria, Italy, generated and used nanoparticles in art fabrication during the Renaissance period. *Applied Physics A: Solids and Surfaces*, Vol.76, pp. 515-525,
- Padeletti, G. & Fermo, P. (2003b). How the masters in Umbria, Italy, generated and used nanoparticles in art fabrication during the Renaissance period. *Applied Physics a-*

- Materials Science & Processing, Vol.76, No.4, (March 2003), pp. 515-525, ISSN 0947-8396
- Padeletti, G. & Fermo, P. (2004). Production of gold and ruby-red lustres in Gubbio (Umbria, Italy) during the renaissance period. *Applied Physics A: Materials Science & Processing*, Vol.79, No.2, (July 2004), pp. 241-245, ISSN 0947-8396
- Padeletti, G.; Ingo, G. M.; Bouquillon, A.; Aucouturier, M.; Roehrs, S. & Fermo, P. (2006). First-time observation of Mastro Giorgio materpieces by means of non-destructive techniques. *Applied Physics A: Materials Science & Processing*, Vol.83, No.4, (Jun 2006), pp. 475-483, ISSN 0947-8396
- Padovani, S.; Puzzovio, D.; Mazzoldi, P.; Borgia, I.; Sgamellotti, A.; Brunetti, B. G.; Cartechini, L.; D'Acapito, F.; Maurizio, C.; Shokouhi, F.; Oliaiy, P.; Rahighi, J.; Lamehi-Rachti, M. & Pantos, E. (2006). XAFS study of copper and silver nanoparticles in glazes of medieval middle-east lustreware (10th-13th century). *Applied Physics A: Materials Science & Processing*, Vol.83, No.4, (Jun 2006), pp. 521-528, ISSN 0947-8396
- Pérez-Arantegui, J. & Larrea, A. (2003). The secret of early nanomaterials is revealed, thanks to transmission electron microscopy. *Trends in Analytical Chemistry*, Vol.22, No.5, (May 2003), pp. 327-329, ISSN 0165-9936
- Pérez-Arantegui, J.; Molera, J.; Larrea, A.; Pradell, T.; Vendrell-Saz, M.; Borgia, I.; Brunetti, B. G.; Cariati, F.; Fermo, P.; Mellini, M.; Sgamellotti, A. & Viti, C. (2001). Luster pottery from the thirteenth century to the sixteenth century: a nanostructured thin metallic film. *Journal of the American Ceramic Society*, Vol.84, No.2, (February 2001), pp. 442-446, ISSN 0002-7820
- Perez-Villar, S.; Rubio, J. & Oteo, J. L. (2008). Study of color and structural changes in silver painted medieval glasses. *Journal of Non-Crystalline Solids*, Vol.354, No.17, (April 2008), pp. 1833-1844, ISSN 0022-3093
- Pichon, L.; Beck, L.; Walter, P.; Moignard, B. & Guillou, T. (2010). A new mapping acquisition and processing system for simultaneous PIXE-RBS analysis external beam. *Nuclear Instruments & Methods in Physics Research, Section B: Beam Interactions with Materials and Atoms*, Vol.268, No.11-12, (Jun 2010), pp. 2028-2033, ISSN 0168-583X
- Pradell, T.; Molera, J.; Bayes, C. & Roura, P. (2006). Luster decoration of ceramics: mechanisms of metallic luster formation. *Applied Physics A: Materials Science & Processing*, Vol.83, No.2, (May 2006), pp. 203-208, ISSN 0947-8396
- Pradell, T.; Molera, J.; Roqué, J.; Vendrell-Saz, M.; Smith, A. D.; Pantos, E. & Crespo, D. (2005). Ionic-exchange mechanism in the formation of medieval luster decorations. *Journal of the American Ceramic Society*, Vol.88, No.5, (May 2005), pp. 1281-1289, ISSN 0002-7820
- Reillon, V. (2008). Caractérisation et modélisation des propriétés optiques des ceramiques lustrées. PhD thesis, Université Pierre et Marie Curie – Paris 6.
- Reillon, V. & Berthier, S. (2006). Modelization of the optical and colorimetric properties of lustred ceramics. *Applied Physics A: Materials Science & Processing*, Vol.83, No.2, (May 2006), pp. 257-265, ISSN 0947-8396

- Reillon, V.; Berthier, S. & Andraud, C. (2010). Optical properties of lustred ceramics: complete modelling of the actual structure. *Applied Physics A: Materials Science & Processing*, Vol.100, No.3, (September 2010), pp. 901-910, ISSN 0947-8396
- Ricciardi, P.; Colomban, P.; Tournié, A.; Macchiarola, M. & Ayed, N. (2009). A non-invasive study of Roman Age mosaic glass tesserae by means of Raman spectroscopy. *Journal of Archaeological Science*, Vol.36, No.11, (November 2009), pp. 2551-2559, ISSN 0305-4403
- Roqué, J.; Molera, J.; Cepria, G.; Vendrell-Saz, M. & Perez-Arantegui, J. (2008). Analytical study of the behaviour of some ingredients used in lustre ceramic decorations following different recipes. *Phase Transitions*, Vol.81, No.2-3, pp. 267-282, ISSN 0141-1594
- Roqué, J.; Molera, J.; Pérez-Arantegui, J.; Calabuig, C.; Portillo, J. & Vendrell-Saz, M. (2007). Lustre colour ans shine from the Olleries xiques workshop in Paterna (Spain), 13th century AD: Nanostructure, chemical composition and annealing conditions. *Archaeometry*, Vol.49, No.3, (August 2007), pp. 511-528, ISSN 0003-813X
- Roqué, J.; Pradell, T.; Molera, J. & Vendrell-Saz, M. (2005). Evidence of the nucleation and growth of the metal Cu and Ag nanoparticles in lustre: AFM surface characterization. *Journal of Non-Crystalline Solids*, Vol.351, No.6-7, (March 2005), pp. 568-575, ISSN 0022-3093
- Rubio, F.; Perez-Villar, S.; Garrido, M. A.; Rubio, J. & Oteo, J. L. (2009). Application of Gradient and Confocal Raman Spectroscopy to Analyze Silver Nanoparticle Diffusion in Medieval Glasses. *Journal of Nano Research*, Vol.8, pp. 89-97, ISSN 1662-5250
- Salomon, J.; Dran, J.-C.; Guillou, T.; Moignard, B.; Pichon, L.; Walter, P. & Mathis, F. (2008). Ion-beam analysis for cultural heritage on the AGLAE facility: impact of PIXE/RBS combination. *Applied Physics A: Materials Science & Processing*, Vol.92, No.1, (July 2008), pp. 43-50, ISSN 0947-8396
- Sciau, P.; Mirguet, C.; Roucau, C.; Chabanne, D. & Schvoerer, M. (2009a). Double nanoparticle layer in the 12th century lustreware decoration: accident or technological mastery. *Journal of Nano Research*, Vol.8, pp. 133-139, ISSN 1662-5250
- Sciau, P.; Salles, P.; Roucau, C.; Mehta, A. & Benassayag, G. (2009b). Applications of focused ion beam for preparation of specimens of ancient ceramic for electron microscopy and synchrotron X-ray studies. *Micron*, Vol.40, No.5-6, (July-August 2009), pp. 597-604, ISSN 0968-4328
- Simmons, C. T. & Mysak, L. A. (2010). Transmissive properties of Medieval and Renaissance stained glass in European churches. *Architectural Science Review*, Vol.53, No.2, (May 2010), pp. 251-274, ISSN 0003-8628
- Smith, A. D.; Pradell, T.; Molera, J.; Vendrell-Saz, M.; Marcus, M. A. & Pantos, E. (2003). MicroEXAFS study into the oxidation states of copper coloured Hipano-Moresque Lustre decorations. *Journal de Physique IV*, Vol.104, (March 2003), pp. 519-522, ISSN 1155-4339
- Watson, O. (1985). Persian lustre ware, Faber and Faber, ISBN 9780571132355, London, UK.

Wood, N. (1999). *Chinese glazes, their origins, chemistry and recreation,* University of Pennsylvania Press, ISBN 978-0-8122-3476-3, Philadelphia, USA.



The Delivery of Nanoparticles

Edited by Dr. Abbass A. Hashim

ISBN 978-953-51-0615-9 Hard cover, 540 pages Publisher InTech Published online 16, May, 2012 Published in print edition May, 2012

Nanoparticle is a general challenge for today's technology and the near future observations of science. Nanoparticles cover mostly all types of sciences and manufacturing technologies. The properties of this particle are flying over today scientific barriers and have passed the limitations of conventional sciences. This is the reason why nanoparticles have been evaluated for the use in many fields. InTech publisher and the contributing authors of this book in nanoparticles are all overconfident to invite all scientists to read this new book. The book's potential was held until it was approached by the art of exploring the most advanced research in the field of nano-scale particles, preparation techniques and the way of reaching their destination. 25 reputable chapters were framed in this book and there were alienated into four altered sections; Toxic Nanoparticles, Drug Nanoparticles, Biological Activities and Nano-Technology.

How to reference

In order to correctly reference this scholarly work, feel free to copy and paste the following:

Philippe Sciau (2012). Nanoparticles in Ancient Materials: The Metallic Lustre Decorations of Medieval Ceramics, The Delivery of Nanoparticles, Dr. Abbass A. Hashim (Ed.), ISBN: 978-953-51-0615-9, InTech, Available from: http://www.intechopen.com/books/the-delivery-of-nanoparticles/nanoparticles-in-ancient-materials-the-metallic-lustre-decorations-of-medieval-ceramics

INTECH

open science | open minds

InTech Europe

University Campus STeP Ri Slavka Krautzeka 83/A 51000 Rijeka, Croatia Phone: +385 (51) 770 447

Fax: +385 (51) 686 166 www.intechopen.com

InTech China

Unit 405, Office Block, Hotel Equatorial Shanghai No.65, Yan An Road (West), Shanghai, 200040, China 中国上海市延安西路65号上海国际贵都大饭店办公楼405单元

Phone: +86-21-62489820 Fax: +86-21-62489821 © 2012 The Author(s). Licensee IntechOpen. This is an open access article distributed under the terms of the <u>Creative Commons Attribution 3.0</u> <u>License</u>, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.