Available online at www.sciencedirect.com

SciVerse ScienceDirect

Journal of the European Ceramic Society 32 (2012) 2825–2830

www.elsevier.com/locate/jeurceramsoc

Development of a yellow ceramic pigment based on silver nanoparticles

S. Mestre [a,*], C. Chiva [b], M.D. Palacios [a], J.L. Amorós [a]

[a] Instituto de Tecnología Cerámica, Asociación de Investigación de las Industrias Cerámicas, Universitat Jaume I, Castellón, Spain
[b] Centro Ceramico Bologna, Via Martinelli 23, Bologna, Italy

Available online 29 December 2011

Abstract

In this study a yellow pigment was obtained for third-fire ceramic decorations, based on silver nanoparticles synthesised by the method of chemical reduction in aqueous phase, using silver nitrate and polyvinylpyrrolidone as raw materials. Monitoring of the nanoparticle synthesis reaction by UV–vis spectroscopy allowed optimum operating conditions to be defined in preparing these particles for use as chromophores. Under these conditions, a stable suspension of Ag nanoparticles, which were well dispersed and had an average diameter of 20–30 nm, was obtained. Polyvinyl alcohol and tetraethyl orthosilicate were then added to the nanoparticle suspension to obtain the pigment precursor. The pigment precursor was directly applied on to fired glazed ceramic tile. Subsequent thermal treatment at moderate temperature (700 °C) yielded a layer less than one micron thick, which generated an intense yellow colour.

Keywords: Powders chemical preparation; Silver nanoparticles; Traditional ceramics; Colour

1. Introduction

Ceramic pigments are the most expensive raw material in ceramic tile manufacture, despite being used in small proportions with relation to the total mass of the product. Pigments are mainly synthesised industrially by the traditional ceramic method, involving reactions between solid raw materials (oxides, carbonates, hydroxides, etc.), high temperatures, and long residence times.[1,2] The method has a number of drawbacks, however, particularly because of the high energy consumption during thermal treatment and in the milling of the end product.

At present, the ceramic industry is directing research into the development of pigments with enhanced colouring strength, cheaper synthesis methods, and alternative raw materials. In recent years, different ceramic pigment synthesis techniques have been developed on a laboratory scale with a view to finding alternatives to the traditional method, as well as to improving the physical and chemical characteristics of the synthesised pigments. These techniques are based for example on coprecipitation,[3,4] spray pyrolisis,[5] the sol–gel method,[6] fused salt synthesis,[7] or solution combustion synthesis.[8] One of the key features of these techniques is the mixing on a molecular level of the raw materials. The results obtained on a laboratory scale suggest that such techniques may be valid alternatives to the traditional ceramic method. Their advantages include fewer process stages, lower synthesis temperatures, control of the product's particle size distribution, and the use of alternative raw materials to solid oxides.

Such alternative raw materials include metallic nanoparticles, whose notable optical properties provide them with significant value in nanoscience and in their particular applications.[9] Their singular optical properties are due to the so-called surface plasmon resonance (SPR) phenomenon, which leads to very strong absorption of certain frequencies of the electromagnetic spectrum. The solution of Maxwell's equations for an electromagnetic wave interacting with small metallic spheres indicates that the SPR depends explicitly on particle size. As the particle size increases, the plasmon band red shifts and the bandwidth increases.[10]

The characteristic SPR absorption corresponds to the visible range in the case of gold, silver, and copper nanoparticles,[11] which generates very intense colorations, so that they may be considered inorganic chromophores.[12] Descriptions may be found of pigments[13] and inks for inkjet printing[14–16] made with gold nanoparticles for obtaining reddish tones, based on this phenomenon.

In the case of silver nanoparticles, SPR produces an intense yellow colour, so that they could be suitable chromophores for synthesising alternative ceramic pigments to the currently available yellow pigments, which exhibit problems of toxicity in the

* Corresponding author. Tel.: +34 964 24 24 24. fax: +34 964 34 24 25.
E-mail address: sergio.mestre@itc.uji.es (S. Mestre).

0955-2219/$ – see front matter © 2011 Elsevier Ltd. All rights reserved.
doi:10.1016/j.jeurceramsoc.2011.12.006

raw materials (this being the case of (V)ZrO_2 and $Pb_2Sb_2O_7$) or of chromophore availability (constraints on the praseodymium supply in the case of (Pr)$ZrSiO_4$[17]).

One of the most appropriate methods of synthesising a silver nanoparticle suspension is by chemical reduction in aqueous phase, because of its simplicity, versatility, and cost.[18] In this process the Ag(I) ions from a silver salt are reduced to Ag(0) in an aqueous medium with an organic reagent. A further agent can also be added to assure nanoparticle suspension stability if the organic reagent does not already perform this function. The nanoparticle synthesis reaction in aqueous phase is usually monitored by UV–vis spectroscopy, taking advantage of the notable changes in colour that the reactant mixture undergoes. Suspension absorbance is usually measured at about $\lambda = 410$ nm, at which the maximum absorption of silver nanoparticles occurs.[19,20] This technique enables the operating conditions under which maximum absorption is obtained in the visible region to be identified, a situation that may be assumed to correspond to the nanoparticles with the greatest colouring strength.

In this study, the optimum conditions for producing a silver nanoparticle suspension that was stable for long periods of time and displayed a highly saturated yellow colour were determined. The solution yielded a liquid precursor that generated an intense yellow decoration on fired glazed ceramic tile. This required introducing additives that prevented the silver nanoparticles from agglomerating and subsequently sintering during the thermal treatment needed to fix the decoration on the fired glaze coating. Glasses have been described in the past that were coloured by devitrified silver nanoparticles,[21] as well as traditional glazes that contained silver and copper nanoparticles (Mediterranean lustre decoration),[22–24] but no reports are available on the use of previously synthesised silver nanoparticles as chromophores in pigments for ceramics.

2. Experimental

The raw materials used to synthesise the silver nanoparticles were $AgNO_3$ (Panreac Química S.A.U., Spain) and a polyvinylpyrrolidone with a molecular weight of 10,000 g/mol (PVP, Sigma–Aldrich GmbH, Germany). The additives used to stabilize the nanoparticles were polyvinyl alcohol (PVA, Mowiol 4-88, Clariant Ibérica Producción, S.A.) and tetraethyl orthosilicate (TEOS, Acros Organics SPRL, Belgium).

The silver nanoparticles were prepared by adapting the method of chemical reduction in aqueous phase. The optimised process started with 350 ml of a 0.0042 M PVP solution, to which 50 ml of a 0.0125 M $AgNO_3$ solution was added. The reactant mixture was introduced into a glass reactor, which was heated with a thermostatted water bath. The mixture was continuously stirred under isothermal conditions for 8 h. When the reaction time had ended, the mixture was allowed to cool to room temperature. During the reaction, liquid samples were extracted at intervals proportional to the reaction rate in order to obtain the absorption curve in the visible region by spectrophotometry, as well as the CIELab coordinates using a CIE standard illuminant D_{65} and a CIE 10° standard observer (Colour-Eye 7000A, X-Rite Inc, USA). Preliminary tests enabled 60 °C to be defined as the most appropriate temperature to carry out the synthesis.

In order to complete the pigment precursor, a 13% by weight solution of PVA in water, corresponding to 60% of the nanoparticle suspension volume, was added to the nanoparticle suspension, the mixture being continuously stirred for 30 min. Eight millilitre TEOS was then added and continuously stirred for a further 60 min.

The resulting solution was immediately applied by airbrushing on to fired glazed red-body ceramic tile. The fired glaze was white. After the airbrush application, each tile was dried in an oven at a temperature of 60 °C for 24 h before subjecting it to a thermal treatment of the third-fire type in a rapid laboratory kiln (Pirometrol S.A., Spain), characterised by a dwell of 15 min at 700 °C.

The CIELab chromatic coordinates of the decorated surfaces were measured with the same spectrophotometer as above, but operating in the reflectance mode.

The crystallite size of the silver nanoparticles was evaluated by X-ray diffraction (XRD) analysis. The XRD diffractograms were obtained from the dried suspension using a Theta-Theta model diffractometer (D8 Advance, Bruker, Germany) with Cu Kα radiation ($\lambda = 1.54183$ Å). The generator settings were 45 kV and 40 mA. The XRD data were collected in a 2θ of 5–90° with a step width of 0.015° and a counting time of 1.2 s/step by means of a VÅNTEC-1 detector. The collected data were used in a Rietveld refinement. The 4.2 version of the Rietveld analysis program DIFFRACplus TOPAS was used, assuming a pseudo-Voight function to describe peak shapes. The refinement protocol included the background, the scale factors and the global-instrument, lattice, profile and texture parameters.

The silver nanoparticles and the microstructure of the resulting decorations were characterised with a field-emission gun environmental scanning electron microscope (FEG-ESEM Quanta 200F, FEI Co, USA), equipped with an energy-dispersive X-ray microanalysis instrument (Genesis 7000 SUTW, EDAX, USA).

3. Results and discussion

The reduction of silver nitrate in aqueous phase generated a liquid with a colour that ranged from saturated yellow to dark brown, depending on the operating conditions. However, when the reaction temperature was held at 60 °C, a suspension with an intense yellow colour was obtained. This suspension remained stable for several weeks, without any visually noticeable changes.

Spectroscopic monitoring of the reaction allowed the gradual appearance of a band located in the 410–430 nm range, corresponding to absorption by the silver nanoparticles owing to the SPR phenomenon, to be observed (Fig. 1). This band exhibited a complex evolution with time. During the first 300 min of the reaction, the band remained well defined, which might indicate that nanoparticles of relatively uniform size were being generated. After this time, however, the band lost definition, which might be caused by the appearance of a wider particle size distribution or agglomeration of the already synthesised

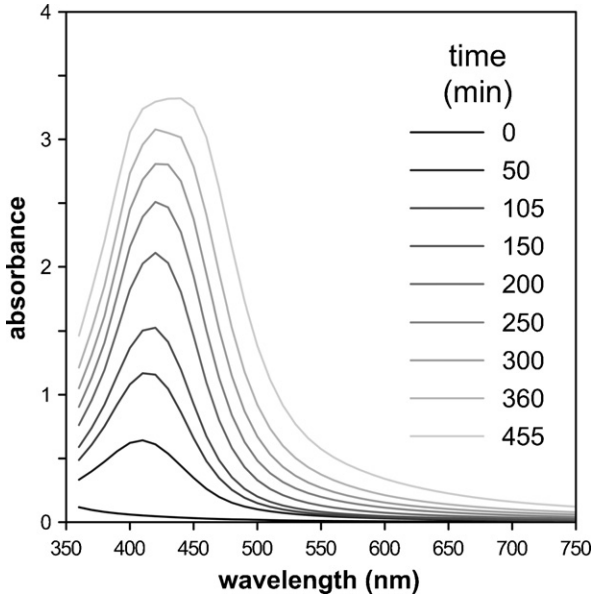

Fig. 1. Evolution of the absorbance curves in the visible region of the reactant mixture with elapsed time.

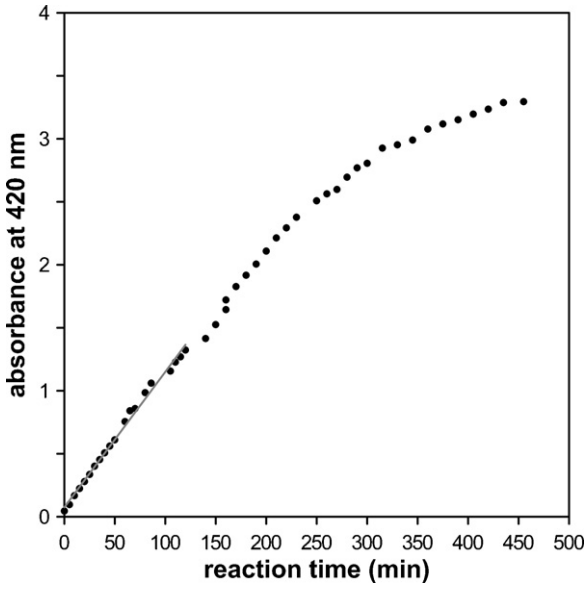

Fig. 2. Evolution of absorbance at 420 nm of the reactant mixture with elapsed time.

nanoparticles. As synthesis progressed, the absorption band maximum shifted from 410 nm to 440 nm, which was also consistent with nanoparticle growth (theoretical calculus for silver nanoparticles in water predicted a maximum in absorbance at 400 nm for particles between 1.5 and 7 nm, maximum that progressively shifts to 460 nm as the radius of the nanoparticles increases up to 40 nm[25]). Since there was a large excess of pyrrolidone with respect to silver (30:1 molar), the reduction of silver was considered to have been completed when reaction time ended.

On selecting the absorbance at 420 nm in order to monitor its evolution during the reaction, it was noted that absorbance increased linearly with time during the first 2 h. After this point, however, the progression stopped, as if an asymptotic trend had started whose limit was not reached during the reaction time (Fig. 2). This behaviour may be interpreted, in accordance with the Lambert–Beer law, by assuming a linear increase in the chromophore concentration in the liquid, which in this case would correspond to the relatively uniformly sized silver nanoparticles. However, after 2 h, chromophore saturation would lead to the observed deviation, which would become more pronounced as the widening of the silver nanoparticle size distribution also contributed to displace the absorption band towards the red end of the spectrum.

The presence of silver nanoparticles from the reaction in the suspension was confirmed by drying a fraction of the suspension and then analysing the resulting dry residue by SEM and DRX. Although the organic matter from the PVP made it difficult to obtain defined images, silver nanoparticles sized between 20 and 30 nm were identified in the residue (Fig. 3), a fraction of which was agglomerated. Only metallic silver was identified by XRD, while other possible phases such as Ag_2O were absent, which is consistent with the assumption that all the silver ions had been reduced. The measurement of silver crystal size indicated that this was 22 ± 4 nm. These results suggest that the particles identified in Fig. 3 were primary crystals of silver, while the small number of agglomerates indicates that the spectrophotometric curve shift was mainly due to nanoparticle growth. On the other hand, the agglomerates did not appear to be linked by solid bridges, so that they might have formed during drying.

The appropriate operating conditions for synthesising the nanoparticles for the yellow pigment were selected by evaluating the chromatic coordinates calculated from the spectrophotometric measurements. The evolution of L^*, a^*, and b^* with reaction time (Fig. 4) indicated that the highest values of the yellow component were obtained at long reaction times (about 350 min). However, when synthesis time was further prolonged, though b^* did not decrease too much, a notably less luminous and somewhat more reddish colour was obtained, which might lead to

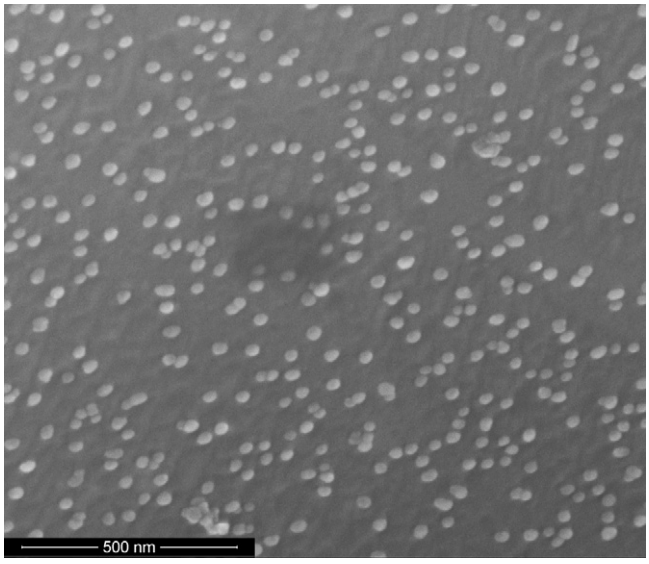

Fig. 3. Photograph of the dry residue of the suspension obtained when the reaction had ended.

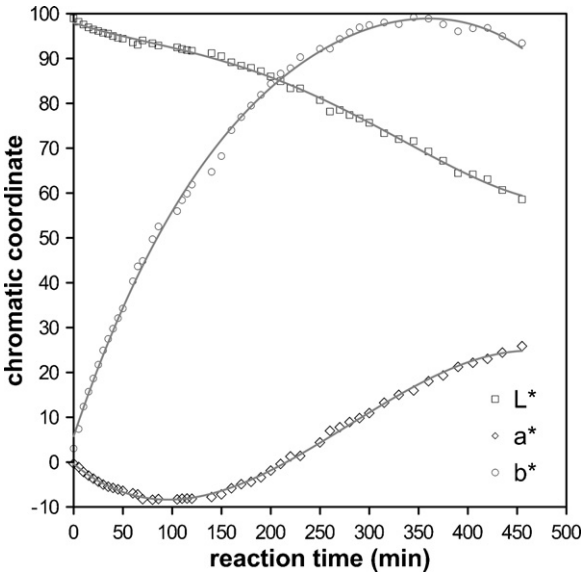

Fig. 4. Evolution of the chromatic coordinates of the reactant mixture with elapsed time.

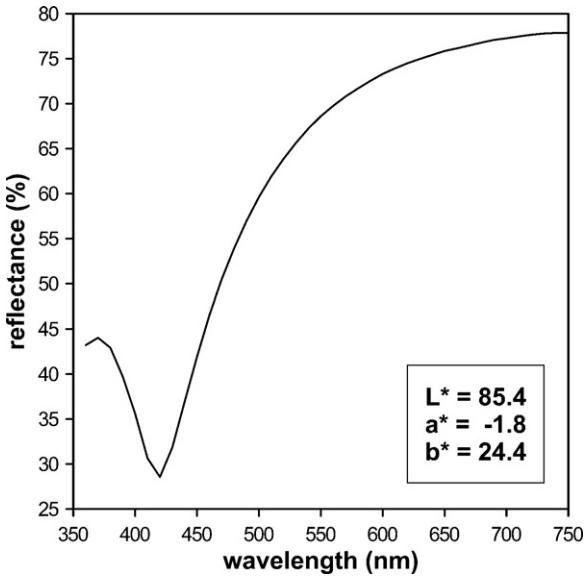

Fig. 5. Reflectance curve and chromatic coordinates of the glaze surface decorated with the synthesised pigment.

a visual impression of a more intense yellow. The operating conditions corresponding to a reaction time of about 8 h were chosen, therefore, to synthesise the nanoparticles that were to act as chromophores in the pigment.

Since the physical characteristics of the silver nanoparticle suspension were inappropriate for the suspension's direct application on to the fired glazed tiles, it was necessary to add PVA as a rheological agent to adjust the viscosity of the solution. This decreased the solution's surface tension and increased its capacity to wet the fired glaze. The PVA and the PVP would also help avoid silver nanoparticle agglomeration during the drying stage. On the other hand, various studies indicate that silver nanoparticles begin to exhibit sintering effects at temperatures of about 150 °C.[26] A small quantity of TEOS was therefore added to the suspension in order to create a silica barrier between the silver nanoparticles during thermal treatment, which would reduce their tendency to sinter as far as possible and also facilitate the integration of the decoration into the fired glaze on which it was deposited. This approach had been successfully applied to obtain a pigment based on gold nanoparticles dispersed inside silica particles.[13] In fact, tests conducted at the laboratory with an analogous suspension to the one described, without a TEOS addition, yielded a final greyish colour, probably because of silver nanoparticle sintering during the thermal cycle once oxidation of the organic additives had ended.

The airbrush application of the synthesised precursor and subsequent thermal treatment gave rise to a glazed surface with a quite intense yellow coloration, which indicated that the pigment had been appropriately synthesised. The reflectance curve in the visible region of this surface exhibited a minimum at 420 nm (Fig. 5), indicating that the silver nanoparticles had, at least partially, survived the thermal treatment. The chromatic coordinates corresponded to an intense yellow colour, which was quite luminous and was comparable to the colours obtained with traditional yellow pigments in third-fire decorations.

The SEM characterisation of the resulting decoration indicated that the layer thickness was quite uniform (700 ± 20 nm, Fig. 6) and that it contained clearly differentiated silver nanoparticles (the results of the microanalysis performed on one of the lighter-coloured spherical particles confirmed the presence of Ag, Fig. 7). The silver nanoparticles in the applied layer exhibited a quite wide size distribution, the presence of particles with a diameter of about 500 nm particularly standing out, in addition to particles that had undergone no variation at all (Fig. 8). The volume percentage of silver in the applied layer was estimated, by image analysis, to range between 16% and 20%. Furthermore, about 20% of that volume consisted of silver particles below 100 nm.

This result may be interpreted by assuming that the additives incorporated into the suspension to avoid agglomeration and sintering of the silver nanoparticles during drying and thermal treatment had only partly achieved their purpose, so that only a fraction of the initial nanoparticles had maintained their individuality. In addition, other mechanisms might have intervened to define the final distribution of silver in the glaze, such as silver nanoparticle growth by Ostwald ripening, the dissolution of silver in the glaze, or silver nanoparticle oxidation to Ag_2O. Independently of the mechanisms involved, the fraction of silver nanoparticles was sufficiently large to enable the yellow

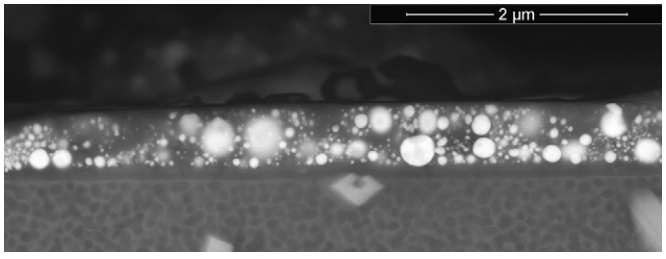

Fig. 6. Polished cross-section of the glaze with the applied pigment layer, in which the spherical chromophore particles may be observed.

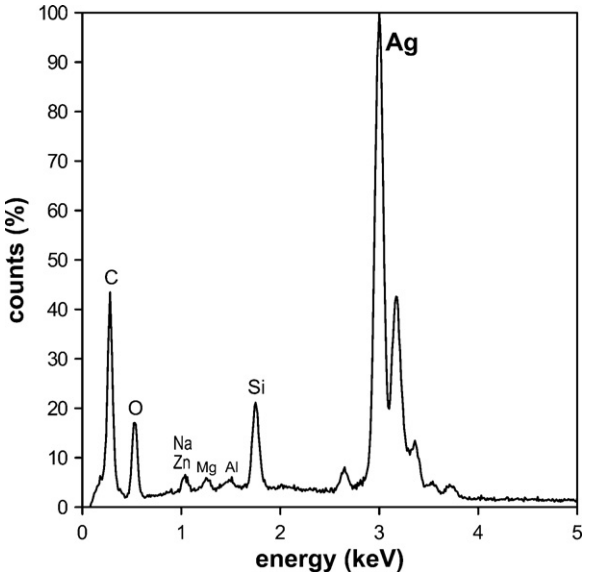

Fig. 7. EDX analysis of a region of the layer displayed in Fig. 6, in which white particles had accumulated, confirming the high silver content.

coloration completely to dominate the appearance of the decorated surface, but it did not achieve the colour saturation observed in the nanoparticle suspension. On the other hand, since a standard yellow pigment-containing fired glaze is easily 300 μm thick, the strong colouring strength of the decoration obtained is particularly to be noted, as the thickness of the deposited layer was about one fifth of the thickness of a typical fired glaze layer.

The results obtained open the way to developing a pigment with even greater colouring strength, if the silver nanoparticle fraction that keeps the initial nanoparticle size in the final decoration on the glaze can be increased.

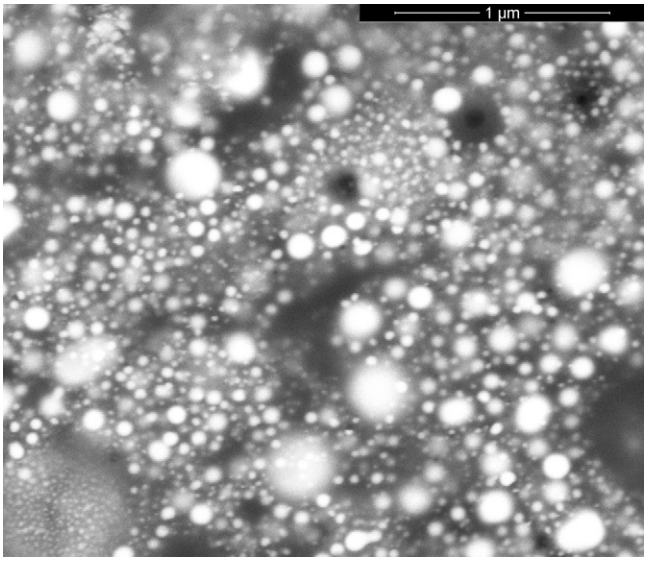

Fig. 8. Surface of the applied layer, showing the notable width of the silver particle size distribution.

4. Conclusions

The optimum parameters for synthesising a stable suspension of silver nanoparticles, with an average diameter of 20–30 nm, were determined using the method of chemical reduction in aqueous phase.

The resulting silver nanoparticle suspension enabled a third-fire pigment precursor to be synthesised, incorporating PVA as a rheological agent and TEOS as a SiO_2 generator, which limited nanoparticle agglomeration and sintering during the drying and firing processes.

A satisfactory third-fire type of decoration on fired glazed ceramic tile was thus obtained: the decoration exhibited an intense yellow colour, with a layer that was much thinner than the thickness required in coatings produced with traditional pigments. However, a part of the nanoparticles initially present in the suspension underwent sintering processes during the thermal treatment, so that their size no longer allowed selective absorption by means of the SPR mechanism.

The research currently being conducted focuses on optimising the precursor, with a view to better protecting the silver nanoparticles. This would allow a greater proportion of these nanoparticles to maintain their individuality throughout the entire decorating process and enable pigment colouring strength to be enhanced.

References

1. Società Ceramica Italiana. *Colore, pigmenti e colorazione in ceramica*. Modena: S.A.L.A. Editore; 2003.
2. Singer F, Singer FF. *Industrial ceramics*. London: Chapman & Hall; 1962.
3. Pishch IV, Radion EV. A pigment based on coprecipitated iron(III) and nickel(III) hydroxides. *Glass Ceram* 1996;**53**:178–9.
4. Pishch IV, Radion EV, Sokolovskaya DM, Popovskaya NF. A pigment based on coprecipitated chromium(III) and copper(III) hydroxides. *Glass Ceram* 1996;**53**:211–3.
5. Mooney JB, Radding B. Spray pyrolysis processing. *Annu Rev Mater Sci* 1982;**12**:81–101.
6. Candeia RA, Souza MAF, Bernardi MIB, Maestrelli SC, Santos IMG, Souza A, et al. $MgFe_2O_4$ pigment obtained at low temperature. *Mater Res Bull* 2006;**41**:183–90.
7. Ouahdi N, Guillemet S, Durand B, El Ouatib R, Er Rakho L, Moussa R, et al. Synthesis of $CoAl_2O_4$ by double decomposition reaction between $LiAlO_2$ and molten $KCoCl_3$. *J Eur Ceram Soc* 2008;**28**:1987–94.
8. Manoharan SS, Patil KC. Combustion synthesis of metal chromite powders. *J Am Ceram Soc* 1992;**75**:1012–5.
9. Evanoff DD, Chumanov G. Synthesis and optical properties of silver nanoparticles and arrays. *ChemPhysChem* 2005;**6**:1221–31.
10. Kelly KL, Jensen TR, Lazarides AA, Schatz GC. Modeling metal nanoparticles optical properties. In: Feldheim DL, Foss Jr CA, editors. *Metal nanoparticles: synthesis, characterization and applications*. New York: CRC Press; 2002.
11. Xia Y, Halas NJ. Shape-controlled synthesis and surface plasmonic properties of metallic nanostructures. *MRS Bull* 2005;**30**:338–48.
12. Sun Y, Sia Y. Gold and silver nanoparticles: a class of chromophores with colors tunable in the range from 400 to 750 nm. *Analyst* 2003;**128**:686–91.
13. Mestre S, Palacios MD. Spanish patent ES2322840. 14/6/2010.
14. García J, Benet C, Fenollosa JL, Querol JM, Secrest P. US patent PCT/US2000/033335. 09/03/2005.
15. Gardini D, Dondi M, Costa AL, Matteucci F, Blosi M, Galassi C, et al. Nanosized ceramic inks for drop-on-demand ink-jet printing in quadrichromy. *J Nanosci Nanotecnol* 2008;**8**:1979–88.

16. Cavalcante PMT, Dondi M, Guarini G, Raimondo M, Baldi C. Colour performance of ceramic nano-pigments. *Dyes Pigments* 2009;**80**:226–32.
17. Service RF. Nations move to head off shortages of rare earths. *Science* 2010;**327**:1596–7.
18. Hoppe CE, Lazzari M, Pardiñas-Blanco I, López-Quintela MA. One-step synthesis of gold and silver hydrosols using poly(N-vinyl-2-pyrrolidone) as a reducing agent. *Langmuir* 2006;**22**:7027–34.
19. Al-Thabaiti SA, Al-Nawaiser FM, Obaid AY, Al-Youbi AO, Khan Z. Formation and characterization of surfactant stabilized silver nanoparticles: a kinetic study, 2008. *Colloid Surf B: Biointerf* 2008;**67**:230–7.
20. Khan Z, Al-Thabaiti SA, Al-Nowaiser FM, Obaid AY, Al-Youbi AO, Malik MA. Kinetics of silver nanoparticle growth in aqueous polymer solutions. *Arab J Chem* 2011, doi:10.1016/j.arabjc.2010.12.024.
21. Barber DJ, Freestone IC. An Investigation of the origin of the colour of the lycurgus cup by analytical transmission electron microscopy. *Archaeometry* 1990;**32**:33–45.
22. Pradell T, Molera J, Bayés C, Roura P. Luster decoration of ceramics: mechanisms of metallic luster formation. *Appl Phys A* 2006;**83**:203–8.
23. Reillon V, Berthier S. Modelization of the optical and colorimetric properties of lustred ceramics. *Appl Phys A* 2006;**83**:257–65.
24. Roqué J, Molera J, Sciau P, Pantos E, Vendrell-Saz M. Copper and silver nanocrystals in lustre lead glazes: development and optical properties. *J Eur Ceram Soc* 2006;**26**:3813–24.
25. Slistan-Grijalva A, Herrera-Urbina R, Rivas-Silva JF, Avalos-Borja M, Castillón-Barraza FF, Posada-Amarillas A. Classical theoretical characterization of the surface plasmon absorption band for silver spherical nanoparticles suspended in water and ethylene glycol. *Physica E* 2005;**27**:104–12.
26. Chou KS, Huang KC, Lee HH. Fabrication and sintering effect on the morphologies and conductivity of nano-Ag particle films by the spin coating. *Nanotechnology* 2005;**16**:779–89.