

PREPARATION AND CHARACTERISATION OF AG COLLOIDS IN CERAMIC MATRICES BY THE SOL-GEL-PROCESS

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A synthesis route for the preparation of Ag colloid containing coatings in SiO_2 , TiO_2 , ZrO_2 and mixed $\text{SiO}_2/\text{TiO}_2$ matrices and $\text{SiO}_2/\text{ZrO}_2$ matrices of different molar ratios has been developed. As a result different, intensely coloured coatings, depending on the refractive index of the matrix, were obtained. In Ag colloid containing mixed $\text{SiO}_2/\text{TiO}_2$ matrices and $\text{SiO}_2/\text{ZrO}_2$ matrices a significant red shift of the peak position wavelength λ_{max} of the Ag plasmon resonance band with decreasing content of SiO_2 was observed and it was possible to adjust λ_{max} of the Ag colloids from yellow (pure SiO_2 matrix: $\lambda_{\text{max}} = 405 \text{ nm}$) to bluish-violet (pure TiO_2 matrix: $\lambda_{\text{max}} = 535 \text{ nm}$ or pure ZrO_2 matrix: $\lambda_{\text{max}} = 530 \text{ nm}$) by the refractive index of the matrix. These results are in good agreement with the calculations obtained from Mie theory for Ag colloid radii of approximately 20 nm.

1. INTRODUCTION

Metal colloids have been used for staining glass¹ for hundreds of years, as known from yellow and ruby coloured church windows containing Ag and Au colloids respectively. From the Mie and Drude² theory it is well known today that the colour of the colloids is due to a surface plasmon resonance effect of the conductive electrons of the colloids, which leads to a selective absorption band in the visible range of light. For small colloids in diluted systems the following equation (1) can be used in order to describe the plasmon resonance condition to a first approximation

$$-\varepsilon_m(\lambda_{\text{max}}) = 2\varepsilon_d(\lambda_{\text{max}}), \quad (1)$$

where ε_m denotes the real part of the dielectric function of the metal colloid, ε_d stands for the dielectric function of the non-absorbing matrix and λ_{max} is the peak position of the surface plasmon effect. For glasses, where ε_d is almost fixed to about $n^2 = 2.25$ ($n = \text{refractive index}$) the peak position of the plasmon resonance is mainly dependent on the dielectric function of the metal. This means that the colour of the composite material is determined by the kind of metal. This has been investigated systematically for Ag in soda-

lime silicate glasses³⁻⁴ and for Au in lead silicate glasses⁵⁻⁶. Sol-gel derived matrices (gels, coatings) are also suitable hosts for metal colloids, but in most cases the formation of Au colloids in low index matrices has been investigated⁷⁻⁹. Sakka¹⁰ described the preparation of Au colloids in sol-gel derived TiO₂ coatings on glass using titanium tetraisopropylate and tetrachloroauric acid as precursors. By dipping and firing at 500 °C Au colloids of about 20 nm were obtained in coatings 80 nm thick. The coatings were coloured blue. The plasmon peak was obtained at around 645 nm wavelength. In a similar manner Ag colloids were prepared in TiO₂ using AgNO₃ as a Ag precursor. After firing at 600 °C, deep violet coloured coatings were obtained. The absorption band showed three peaks at 400 nm, 460 nm and 580 nm, which were attributed to size distribution effects. These results clearly indicate that remarkable red shifts at the surface plasmon band of metal colloids can be obtained by incorporation in high refractive index matrices, however systematic investigations have not yet been performed.

Therefore, the aim of this paper was to prepare metal colloids in coatings with different refractive indices. As matrix materials SiO₂/ZrO₂ and SiO₂/TiO₂ of different molar ratios were chosen. Ag was selected as a metal colloid, because Ag colloids exhibit absorption bands, which are much narrower than those of all other noble metals¹¹. Furthermore, the interband transitions of Ag colloids are located in the UV range and do not interfere with the plasmon resonance in the VIS region as observed for Au or Cu. Therefore interesting colouring effects could be expected by following this approach. Synthesis routes for Ag colloids in SiO₂ coatings¹² and SiO₂/PbO coatings¹³ on glass were used as starting point for this work.

2. EXPERIMENTAL

For the preparation of pure SiO₂ coatings and the mixed SiO₂/TiO₂ coatings and SiO₂/ZrO₂ coatings, AgNO₃ was dissolved in ethanol by ultrasonic treatment for 10 minutes. Then 3-aminopropyltrimethoxysilane (APTS) with a molar ratio of Ag⁺ : APTS = 1:2 was added. Afterwards a prehydrolyzed 3-glycidoxypropyltrimethoxysilane (GPTS) / tetraethylorthosilicate (TEOS) solution with a molar ratio of GPTS : TEOS = 4:1 in ethanol was added under stirring at room temperature¹⁴. For the preparation of mixed SiO₂/TiO₂ coatings and SiO₂/ZrO₂ coatings an appropriate quantity of Ti-butylate or Zr-propylate in ethanol was added dropwise to this solution. In case of Ag containing pure TiO₂ coatings and ZrO₂ coatings, ethylenediamine (EDA) was added to an

ethanolic solution of AgNO_3 in a molar ratio of $\text{Ag}^+ : \text{EDA} = 1:2$ and solutions of Ti-butylate or Zr-propylate in ethanol were added dropwise under stirring at room temperature. The Ag concentrations were adjusted so as to obtain 18.6 mole% of Ag in the $\text{SiO}_2/\text{TiO}_2$ system and 9.3 mole% of Ag in the $\text{SiO}_2/\text{ZrO}_2$ coatings. After stirring the sols for 5 minutes at room temperature, borosilicate glass substrates were dip coated at a withdrawal speed of 2 mm/s and dried at 90 °C for 15 minutes. The coatings were densified for 1 h in reducing atmosphere (8 vol% H_2 , 92 vol% N_2) using heating and cooling rates of about 100 K/h. In addition, Ag-free reference coatings were prepared for each matrix composition, by exactly the same synthesis route, only omitting the addition of the Ag salt. The absorption of the coatings was measured by UV/VIS spectroscopy (Omega 20, Bruins Instruments) and calculated according to Mie theory using a numeric programme¹⁵ and data of the dielectric function of Ag¹⁶. The refractive indices and thicknesses of the Ag-free reference coatings were determined by spectroscopic ellipsometry (ES4G ellipsometer, SOPRA). The measurements were performed at constant angle of incidence and the thicknesses were determined for wavelengths > 500 nm, where the coatings did not absorb, using the Cauchy dispersion model.

3. RESULTS AND DISCUSSION

3.1 Synthesis development

The stabilisation of the Ag^+ in the sols by APTS and EDA respectively was necessary in order to avoid spontaneous precipitation of metallic silver in the ethanolic solution. After dip-coating and drying at 90 °C for 15 minutes in air, transparent and colourless coatings were obtained, indicating that Ag was still present in the ionic state. In order to avoid the formation of Ag_2O during the thermal densification of the coatings¹² firing was performed in reducing atmosphere at 500 °C, resulting in intensely coloured Ag colloid containing coatings with thicknesses in the range of 40 nm to 120 nm. The colour of the prepared coatings changed from yellow (pure SiO_2 matrix) via amber and ruby ($\text{SiO}_2/\text{TiO}_2$, $\text{SiO}_2/\text{ZrO}_2$) to reddish-violet in the case of a pure ZrO_2 matrix and similarly to bluish-violet in the case of a pure TiO_2 matrix. In the case of SiO_2 , colourless Ag-free reference coatings were obtained, but with increasing amounts of TiO_2 or ZrO_2 , the Ag-free reference coatings showed an increasing brownish-grey appearance after

densification in reducing atmosphere. This colouring can be attributed to different causes such as traces of residual carbon (different chain length of the alkoxides employed: Si, Zr and Ti), formation of Ti^{3+} (Ti_2O_3 is black¹⁷) and interference effects. It seems not suitable to conclude that the same discolouring effect is obtained in the Ag containing coatings, because of the different redox behaviour caused by the metallic compound and the NO_3^- . In order to overcome this principle difficulty, alternative preparation routes using different Ag sources, matrix precursors and reducing agents have to be developed. Therefore the reference samples were only used for the ellipsometric determination of thickness and refractive index of the coating but not for the discussion of the absorption spectra of the Ag colloid containing coatings, which will be reported in the next chapter.

3.2 Optical properties

The main aim of this paper was to investigate the optical properties of Ag colloids in matrices with different refractive index. Therefore, the absorption of the coatings was measured by UV/VIS spectroscopy. FIGURE 1 shows the absorption spectra of the Ag colloid containing SiO_2 coatings, TiO_2 coatings and mixed SiO_2/TiO_2 coatings (18.6 mole% Ag) on borosilicate glass after thermal densification at 500 °C in reducing atmosphere.

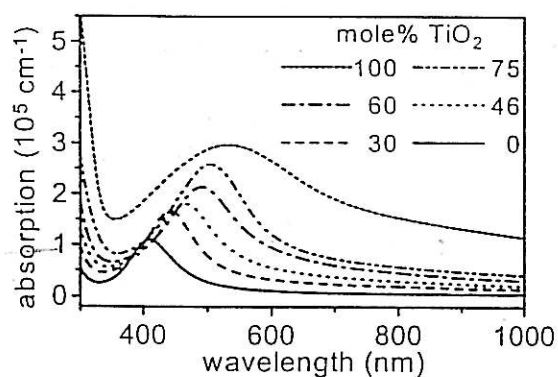


FIGURE 1

UV/VIS spectra of Ag colloids in mixed SiO_2/TiO_2 coatings (double-sided) of different molar ratios on borosilicate glass after 1 h at 500 °C in reducing atmosphere (Ag content: 18.6 mole%).

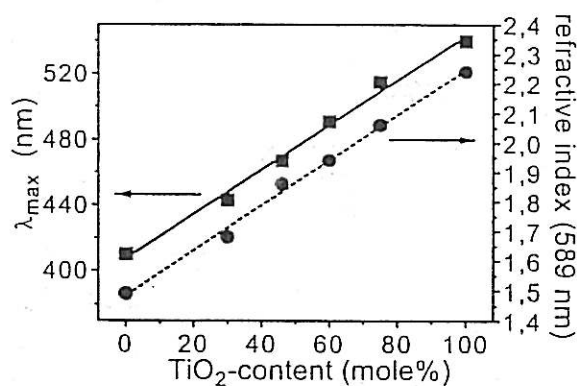


FIGURE 2

Dependence of the refractive index and λ_{max} on the TiO_2 content in mixed SiO_2/TiO_2 matrices of the investigated systems in FIGURE 1.

As can be observed from FIGURE 1, the plasmon peak of the Ag colloids is red shifted from 405 nm (pure SiO₂ matrix) to 535 nm (pure TiO₂). This red shift is shown once again in FIGURE 2, where the position of the measured plasmon peak λ_{\max} and the refractive index n_D , measured at 589 nm wavelength for the Ag-free reference coatings are plotted versus the TiO₂ content of the coatings. As can be seen, λ_{\max} and n_D increase linearly with the TiO₂ content, indicating a strong correlation between λ_{\max} and n_D . The area beneath the absorption curve increases at the same time. It is obvious that the absorption at 1000 nm (i. e. far away from the plasmon peak) also increases with increasing TiO₂ content. This may be due to increased reflectivity, interference phenomena or absorption of residual carbon as discussed in chapter 3.1. The difference between the band for 75 mole% TiO₂ and 100 mole% TiO₂ is remarkable. For the pure TiO₂ matrix a very broad absorption throughout the whole visible range is obtained, which is in a good agreement to the result of Sakka¹⁰ who prepared Ag colloids in TiO₂ coatings under similar conditions. For all SiO₂ containing coatings much narrower bands are obtained. It may be assumed that the different kind of Ag complex formation in SiO₂ containing coatings (using APTS) and in the TiO₂ coating (using EDA) could cause different nucleation and therefore the difference in the spectra of SiO₂ containing coatings and TiO₂ coatings might be due to size effects (formation of larger colloids in TiO₂). In order to prove this hypothesis, the absorption spectra of the prepared systems were calculated for different colloid sizes and the λ_{\max} values of the calculated bands were determined graphically. The result is shown in FIGURE 3.

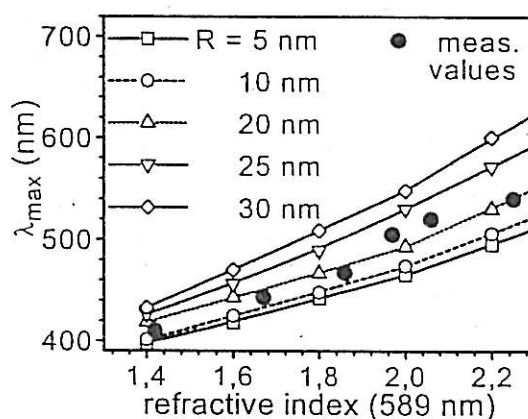


FIGURE 3

Calculated λ_{\max} values of Ag colloids with different sizes in matrices of different refractive indices n_D compared with λ_{\max} values of Ag colloids in the prepared SiO₂/TiO₂ coatings.

FIGURE 3 shows that the calculated λ_{\max} values are continuously red shifted for increasing refractive index, which is in good agreement with the experimental results shown in FIGURE 2. Furthermore it can be seen that the peak positions of the measured bands are quantitatively in good agreement with those of spectra calculated for particles with radii between 10 and 20 nm (for TiO_2 contents of up to 60 mole% or n_0 up to 1.9, comparing FIGURE 2 and 3) and radii of about 20 nm for 75 mole% and 100 mole% TiO_2 .

However, the half widths of the measured spectra were about 2 times of the values of the corresponding calculated ones. Measured spectra of Au colloids in glasses and coatings are in excellent accordance with the calculations, so that deviations caused by the numeric programme can be excluded. Especially for pure TiO_2 ($n_0 = 2.3$) a large misfit of 300 nm (measured) to 140 nm (calculated for 20 nm radius) was obtained. The half width strongly depends on the damping of the plasmon resonance, which is influenced by the particle size (mean free-path effect) but also by interfacial effects¹⁸. In order to explain this misfit, further investigations will be necessary.

In this context, it was interesting to investigate the optical properties of the Ag colloids in the $\text{SiO}_2/\text{ZrO}_2$ system. FIGURE 4 represents the absorption spectra of the double-sided Ag colloid containing $\text{SiO}_2/\text{ZrO}_2$ coatings (9.3 mol% Ag) with different molar ratios on borosilicate glass after densification at 500 °C in reducing atmosphere.

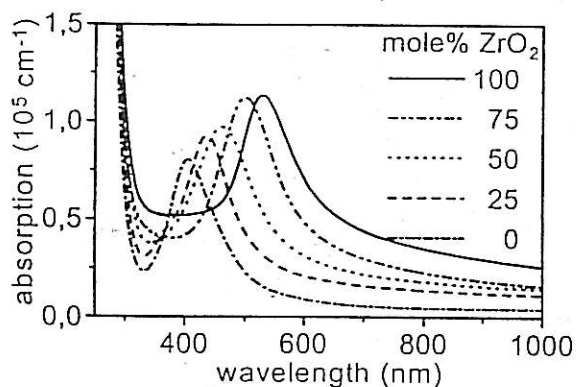


FIGURE 4

UV/VIS spectra of Ag colloids in mixed $\text{SiO}_2/\text{ZrO}_2$ coatings (double-sided) of different molar ratios on borosilicate glass after 1 h at 500 °C in reducing atmosphere (Ag content: 9.3 mol%).

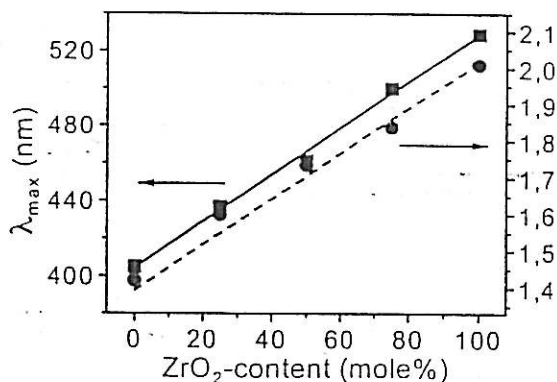


FIGURE 5

Dependence of the refractive index and λ_{\max} on the ZrO_2 content in mixed $\text{SiO}_2/\text{ZrO}_2$ matrices of the investigated systems in FIGURE 4.

As can be seen from FIGURE 4, the spectra of the Ag colloids in the $\text{SiO}_2/\text{ZrO}_2$ system are qualitatively in good agreement with those of Ag colloids in the $\text{TiO}_2/\text{SiO}_2$ system. The red shift of λ_{max} is well correlated to the increasing refractive index of the coating as shown in FIGURE 5. Again the absorption at 1000 nm increases with increasing ZrO_2 content. On the other hand the absorption bands in the ZrO_2 system are narrower compared to the TiO_2 containing coatings. The results of the calculated spectra are presented in FIGURE 6.

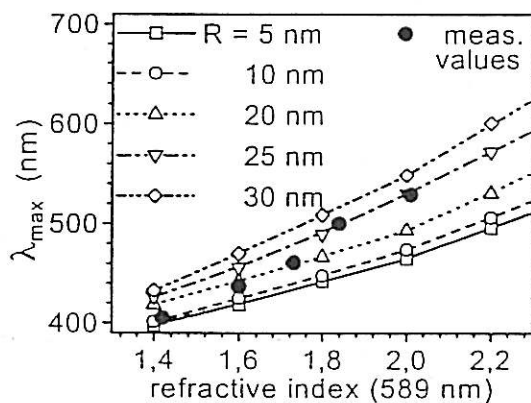


FIGURE 6

Calculated λ_{max} values of Ag colloids with different sizes in matrices of different refractive indices n_D compared with λ_{max} values of Ag colloids in the prepared $\text{SiO}_2/\text{ZrO}_2$ coatings.

FIGURE 6 clearly shows that the peak position of the calculated spectra is red shifted significantly with an increasing refractive index of the matrix. This is in a very good agreement with the results of the measurements. FIGURE 6 indicates that the average colloid size increases with increasing refractive index of the matrix (e. g. increasing ZrO_2 content) from about 10 nm to about 25 nm. It is assumed that this is due to an influence of the matrix composition on nucleation and growth of the Ag colloids during thermal densification of the matrix under the chosen process parameters.

4. CONCLUSION

The theoretical and experimental results lead to the following conclusion: The synthesis of Ag colloids in $\text{SiO}_2/\text{TiO}_2$ matrices and $\text{SiO}_2/\text{ZrO}_2$ matrices with different molar

ratios allows coatings to be prepared on glass with different intense colours. The peak positions of the appropriate absorption bands (and therefore the colours of the coatings) are mainly controlled by the refractive index of the matrix but interfacial effects have to be taken into consideration, which lead to rather broad absorption bands. Further investigations of the growth kinetics of the colloids with different temperature / time programmes in combination with electron microscopic characterisations will be necessary to prove this hypothesis.

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