

Organic nanocrystals grown in sol–gel coatings

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Well-defined organic crystals have been grown in inorganic gel coatings with particle sizes in the submicron range and narrow size distributions. The direct characterisation of these hybrid organic–inorganic films by optical confocal microscopy has allowed elucidation of the role of the main experimental parameters such as the nature of the gel precursors or solvents, the organic doping level and the rotation speed of the spin-coating apparatus. This is a one-step process in which nucleation and growth of the organic crystals occur simultaneously with the formation of the gel framework. Nanocrystallisation is optimised through the control of the coupling effect between the three elementary processes: nucleation, growth and matrix polymerisation. The validity and reproducibility of this simple and generic method have been demonstrated through the use of several organic molecules, solvents and silicon alkoxides.

Introduction

The need for new optically functional materials increases with the expansion of their optical applications. Thus, nanoscale optical research is a highly active field as the properties of nanocrystals are intermediate between those of crystals and molecules, due to quantum size and surface enhancement effects. In this area, a great interest is focussed on the study of inorganic nanocomposite materials^{1,2} while the study of organic nanocrystals has attracted little attention^{3,4} due to their low stability and the difficulties associated with their structural characterisation. Nevertheless, organic molecules exhibit interesting spectroscopic properties which can be utilised in lasers, nonlinear optical materials or luminescent solar concentrators^{5,6} for example. These properties are associated with a great flexibility of organic synthesis which stimulates the search for new molecules and applications.

On the other hand, since 1984,⁷ it has been widely shown that the sol–gel method can be used to encapsulate organic molecules in inorganic matrices (bulk or thin films). The flexibility of sol–gel chemistry and the ability to prepare an inorganic matrix close to room temperature are compatible with a wide variety of dyes. Until now, molecules were dispersed within or grafted onto sol–gel networks.^{7–9}

In our work, the molecules form aggregates through the confined nucleation of the organic phase in the pores of the gel matrix. Indeed, in order to increase the stability of the dyes, to allow convenient processing and shaping and to take advantage of the optical properties of organic materials at the nanometer scale, we have recently prepared organic nanocrystals within sol–gel glasses.¹⁰

In this paper, a novel method of preparing organic nanocrystals within sol–gel thin films is reported. The relationship between the aggregation of the organic phases and processing conditions as well as the mechanism of formation are discussed.

Experimental

Preparation of sol–gel coatings

The sol–gel films were prepared by spin-coating. In order to clarify the role of the host network in the nanocrystallisation of the organic molecules, several silicon alkoxide precursors have been used in this work and are listed in Table 1. Thus, thin films are obtained from TMOS, TEOS and 1:1 mixtures of TMOS+MTMOS alkoxides. The sols are synthesised under acid (HCl, pH ≈ 1.5) catalysed conditions by the one step hydrolysis and condensation of the alkoxide precursors with 1 H₂O molecule per –OR function ($h = [\text{H}_2\text{O}]/[-\text{OR}] = 1$). Depending on the organic molecules involved in the process, various solvents such as methyl or ethyl alcohols, and tetrahydrofuran (THF) have been used to dissolve the dye and mix water of hydrolysis with alkoxide precursors with the molar ratio, solvent : alkoxide, $s = 5$ for all the thin films studied here. These solutions are introduced with the organic molecules in airtight cells and annealed at 80 °C for 10 hours in order to obtain homogeneous sols. The sols are then aged at room temperature for several days to allow the hydrolysis and condensation reactions to progress. Aging is necessary to obtain high quality films, to ensure the control of particle growth and to avoid nanocrystal coalescence. In order to allow easy deposition of transparent films onto substrates from sols of low viscosity, the molar ratio was adjusted to 5. The resulting sols were then deposited by spin-coating onto cleaned

Table 1 Abbreviations of silicon alkoxides used in the preparation of the sol–gel coatings

Silicon alkoxides	Chemical formula	Abbreviation
Tetramethoxysilane	Si(OCH ₃) ₄	TMOS
Methyltrimethoxysilane	CH ₃ Si(OCH ₃) ₃	MTMOS
Tetraethoxysilane	Si(OC ₂ H ₅) ₄	TEOS

microscope slides (around 0.3 cm³ of solution deposited on 2.5 × 2.5 cm slides) with speeds of rotation ranging between 500 and 4000 rpm, films 2–0.7 μm thick have been prepared. These nanocomposite coatings are then stabilised by annealing under inert gas at temperatures just below the melting point of the dye.

In order to demonstrate the validity and the flexibility of our nanocrystallisation process, we have grown nanocrystals of several organic phases such as 4-(diethylamino)-β-nitrostyrene (DEANST) and α-[(4'-methoxyphenyl)methylene]-4-nitrobenzene-acetonitrile (CMONS) chosen for their luminescent and nonlinear optical properties.^{11,12} We have also grown nanocrystals of naphthalene in order to show the gain in stability of the organic phase through our nanocrystallisation process as the pure naphthalene crystals exhibit a high sublimation rate. The concentration of the organic phase depends on its solubility in the corresponding solvent and on the nature of the host matrix. The doping level can be expressed as the molar ratio $d = \text{organic}/\text{alkoxide} \approx 10^{-3} - 10^{-1}$. In this study, we have adjusted the experimental conditions to obtain particles of sizes ranging between 100 and 500 nm in order to facilitate their observation by optical confocal microscopy. Smaller organic nanocrystals can also be prepared using this procedure (see next section).

Optical confocal microscopy

The aim of confocal microscopic imaging is to prevent out-of-focus photons from ever contributing to the image.¹³ This is achieved first by illuminating the specimen with a diffraction-limited spot of light, produced by demagnifying a laser-illuminated aperture placed in a conjugated plane of the objective lens focal plane. Those photons emitted or deflected in the volume of the illuminated focal spot of light are then detected point by point with a photomultiplier during the scanning of the sample. Those photons arising from out-of-focus regions are prevented from reaching the detector by placing an imaging aperture in front of it, in a position confocal with the illuminated point within the specimen. In common with other forms of object plane scanning microscopes, an image is generated by raster-scanning a given field of the specimen with the illuminating spot, digitising the analogue output from the photomultiplier to create the digital image pixels, and displaying the resultant digital image on a monitor.

Confocal scanning optical microscopy presents the following main advantages:

- (1) Almost complete elimination of out-of-focus blur in fluorescence or reflection imaging.
- (2) Improved lateral and axial resolutions (basically 0.2 μm lateral resolution and 0.8 μm axial resolution).

DEANST nanocrystals were visualised through fluorescence confocal microscopy: excitation by the 630 nm ray of a 5 mW He–Ne laser, beam splitting by a 655 nm dichroic mirror, emission selection with a 660 nm long-pass filter. In the case of CMONS, the 488 nm ray of a 15 mW argon laser excited the fluorescence, the beam was split by a 510 nm dichroic mirror and the emission was selected with a 515–565 nm band-pass filter.

On the other hand, the naphthalene nanocrystals were observed by reflection confocal microscopy: the light source was the 488 nm ray of a polarised argon laser (15 mW), the beam was split by a semi-reflective mirror and the parasite light, reflected by optical parts, was cancelled out by placing a cross polar filter in front of the detector.

The confocal microscopy images have been analysed by NIH software in order to quantify particle size and size distribution.

Coating surface characterisation

The characterisation of the surface of the gel coating was carried out by atomic force microscopy (AFM) using a

Burleigh Aris-300 microscope. We work under the contact mode with an ultrafine silicon tip with a small cone angle less than 20° and a curvature radius less than 10 nm.

Results and discussion

The crystalline state of the organic aggregates was characterised by their melting points, clearly evidenced by differential scanning calorimetry. However, diffraction peaks were not recorded by the X-ray diffraction methods. This is due to the weak atomic factors of X-ray scattering of the organic phase compared to the inorganic matrix. In addition, the small sizes of the crystals broaden the diffraction peaks and reduce significantly their maximum intensities. In the preparation of organic nanocrystals grown in bulk xerogels as described elsewhere,¹⁰ the polymerisation of the silicate matrix, the confined nucleation of the organic phase in the pores of the gel and the particle growth are well-separated steps. Indeed, matrix gelation is first allowed to occur and then because of the slow diffusion of the molecules in the dense gel medium, the growth rate becomes negligible compared to that of nucleation. This decouples nucleation and particle growth.

On the other hand, in the preparation of nanocomposite thin films, nucleation and growth of the organic phase begins in the viscous sol at the first stage of the coating process, when the drops of solution are spread on the substrate. The fast evaporation of the solvent leads to an instantaneous high supersaturation of the organic phase which is associated with the inorganic polymerisation of the silicate network. We have a one step process since nucleation and growth of the organic crystals occur simultaneously with the formation of the gel framework. At the final stage of the film formation, the dense gel network prevents coalescence of the organic nanocrystals. Thus, the preparation of films involves the coupling of matrix gelation, nucleation and growth. The preparation of our nanocomposite coatings requires control of this coupling. A wide distribution of particle size generally arises from nucleation over a relatively long period of time, when young nuclei are produced during the growth of older nuclei. Here, in order to obtain crystals of a narrow size distribution, we take advantage of high supersaturation to produce instantaneous nucleation. Indeed, the rapid evaporation of the solvent induces the germination of a high number of nuclei. This sudden nucleation quickly lowers the concentration of the molecularly dispersed dye below the critical concentration for self-nucleation, so only a single “burst” of nuclei occurs.¹⁴

Processing of nanocomposite coatings is controlled by the nature of the sol–gel precursors, the dye concentration, the nature of the solvent and its volatility and the rotation speed of the spin-coating apparatus. Studies of the coating conditions and the characterisation of the dye aggregation in the gel-films by optical confocal microscopy allowed us to specify the role played by each of these parameters. In this study, we have mainly adjusted the experimental coating conditions in order to obtain crystal sizes ranging between 100 and 400 nm and to easily characterise the nanocomposite deposits. Nevertheless, lower particle sizes can be obtained with this method, less than 100 nm (Figs. 4(a) and 4(b); see later).

The first experiments were realised with typical TMOS and TEOS gel precursors. TMOS was then selected because its rate of polymerisation (hydrolysis and condensation) is faster than that of TEOS¹⁵ and correlates with the high nucleation and growth rates of the dye. When TMOS (or TEOS) is used as a single precursor the resulting gel network exhibits silanol functions which can form hydrogen bonds with the organic molecules. For example, silanols can form Si–O–H···O–N linkages with the nitro groups of DEANST molecules. These interactions between molecules and the host silicate network disturb the dye aggregation as illustrated in Fig. 1(a). In order

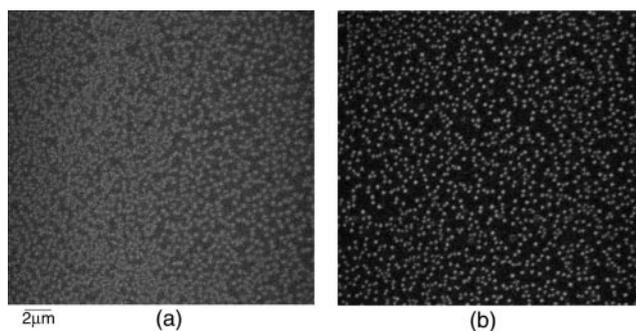


Fig. 1 Optical confocal microscopy photographs of DEANST nanocrystals dispersed in a spin-coating film prepared from (a) TMOS and (b) an equimolar mixture of TMOS + MTMOS alkoxides. In these two experiments the solvent was ethyl alcohol ($s=5$), the doping rate of DEANST $d=2 \times 10^{-2}$ and the rotation speed $r=4000$ rpm.

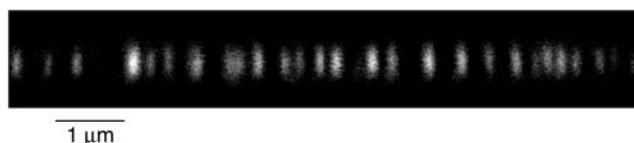


Fig. 2 Cross-section of the film corresponding to Fig. 1(b). The oval shape of the DEANST particles is due to the worse axial resolution compared to the lateral case.

to promote molecular aggregation by decreasing dye–matrix interactions, MTMOS alkoxide was added to TMOS. Equimolar TMOS + MTMOS mixtures lead to ORMOSIL (organically modified silicate) coatings of high optical quality.¹⁵ The non-bridging methyl substituents of MTMOS cover the gel pores^{16,17} and prevent the formation of hydrogen bonds between the silanol of the silicate network and the molecules. This facilitates the nanocrystallisation of the organic molecule as shown in Fig. 1(b). Well-defined nanocrystals are homogeneously dispersed in the gel-film and have a rather narrow size distribution (diameter: 300 ± 20 nm). They form a particle monolayer that is well embedded in the centre of the coating (Fig. 2). This is certainly related, through the solvent evaporation, to the relatively high density of the gel network near the air–film interface at the beginning of the coating process. This higher density of the matrix prevents the nucleation of the dye near the interface due to an increase in the solution boundary. Thus, the organic particles can be stabilised by the inorganic matrix as in the case of naphthalene (see below, Fig. 7) which exhibited no significant sublimation of the nanocrystals over several months. In addition, the lack of organic nanocrystals at the surface of the coating leads to a very low roughness of around 10–20 Å. This good surface quality, as evidenced by atomic force microscopy (Fig. 3), is

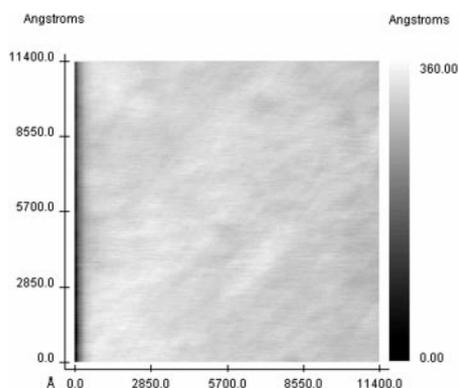


Fig. 3 Atomic force microscopy image of the surface of a film similar to that characterized in Fig. 6(a), the CMONS nanocrystal radii are centered around 100 nm.

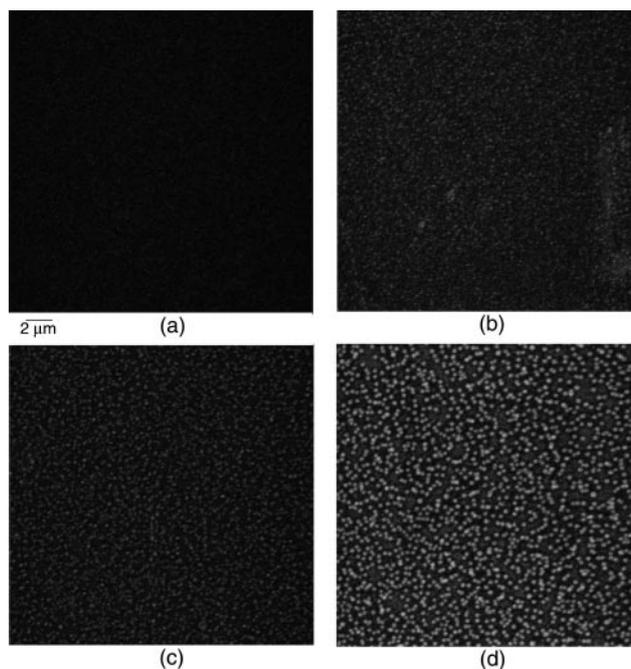


Fig. 4 Confocal microscopy images of DEANST nanocrystals dispersed in TMOS + MTMOS gel films with ethyl alcohol ($s=5$) and $r=4000$ rpm. Several doping rates of DEANST have been used: (a) 0.5×10^{-2} , (b) 1×10^{-2} , (c) 1.5×10^{-2} and (d) 2×10^{-2} leading to a particle radius less than 100 nm for experiments (a) and (b) and centered around 100 nm and 300 nm for experiments (c) and (d) respectively.

essential for the fabrication of wave-guide structures with low losses.

A second set of experiments was carried out by varying only the dye concentration expressed by the molar ratio $d = \text{organic}/\text{alkoxide}$ (Fig. 4). The size of the particles increases with the doping level, d , while the aggregate density remains constant. When d is increased, the critical concentration for nucleation is reached more rapidly through the solvent evaporation and nucleation occurs early compared to the polymerisation of the silicate network. This allows more time for crystal growth and results in larger particle sizes.

Another important parameter of the nanocrystallisation process is the nature of the solvent. For example, the DEANST–gel interface is better defined when methyl alcohol is used (Fig. 5(a)) than when ethyl alcohol is used (Fig. 5(b)). This could be due to the higher volatility of methyl alcohol and hence the greater supersaturation which favours the sudden nucleation. In addition, in the case of ethanol the polymerisation of the silicate network is disturbed by the transesterification reaction¹⁵ which takes place simultaneously with the

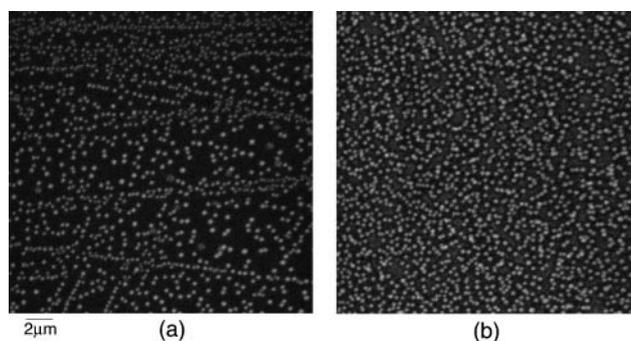


Fig. 5 Confocal microscopy photographs of DEANST aggregates embedded in gel coatings using (a) methyl alcohol and (b) ethyl alcohol solvents. The other experimental parameters are constant: 1:1 TMOS + MTMOS mixture of gel precursors, $d=2 \times 10^{-2}$ and $r=4000$ rpm. The crystal radii are centred around 300 nm.

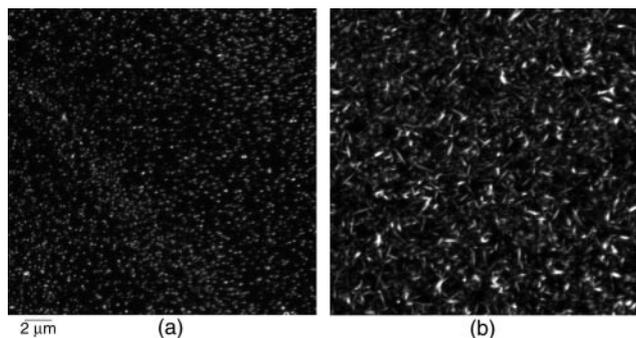


Fig. 6 Comparison by confocal microscopy of two crystallizations of CMONS which are carried out in 1 : 1 TMOS+MTMOS gel coatings and using $r=4000$ rpm: (a) with methyl alcohol solvent, $d=1 \times 10^{-3}$ and $r=4000$ rpm, (b) with THF solvent, $d=4 \times 10^{-3}$ and $r=4000$ rpm.

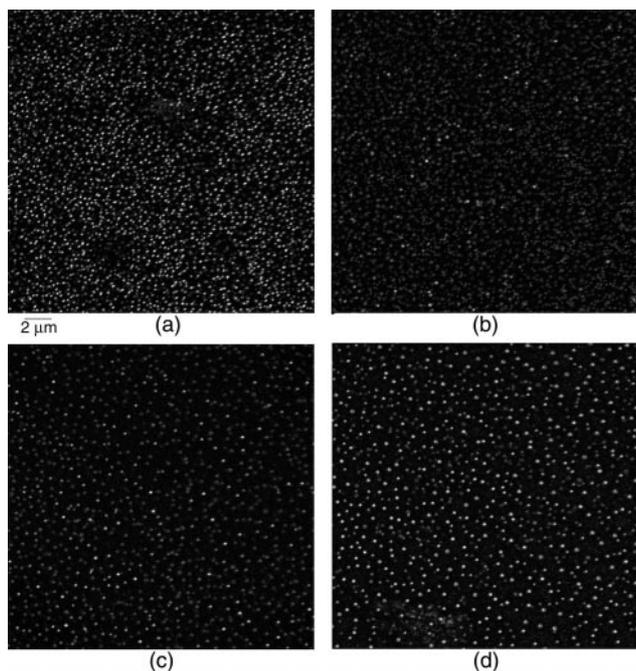


Fig. 7 Effect of the rotation speed, r , on the aggregation of naphthalene in coatings prepared from 1 : 1 TMOS+MTMOS gel precursors with ethyl alcohol and $d=1.10^{-1}$. (a) $r=4000$ rpm and crystal radius $cr \approx 250$ nm, (b) $r=2000$ rpm, $cr \approx 300$ nm (c) $r=1000$ rpm and $cr \approx 350$ nm, (d) $r=500$ rpm and $cr \approx 350$ – 500 nm. Some of the naphthalene nanocrystals appear to be hollow due to the scanning reflection mode where only the surfaces of the nanocrystals are visualized in this case.

hydrolysis and condensation of the silicon alkoxides and delays matrix densification. For the CMONS molecule, methyl alcohol is a good solvent (Fig. 6(a)) for nanocrystallisation. In contrast, convenient nanocrystallisation conditions have not been found with THF, Fig. 6(b). In the latter case, strong interactions between THF and CMONS may disturb the dye aggregation.

The last of the experimental parameters investigated was the rotation speed of the spin-coating apparatus. When the rotation speed is lowered, the rate of solvent evaporation is reduced. Thus, the rate of supersaturation decreases and the formation of the gel framework slows. This increases the duration of the process and leads to a rise in particle sizes and

the size distribution as illustrated in Fig. 7 where naphthalene crystals have been grown using rotation speeds ranging between 4000 and 500 rpm.

Conclusions

In this paper we have described the preparation of a new type of hybrid nanocomposite coating for optical applications. The use of various organic molecules, solvents and silicon alkoxides demonstrates the validity of this simple and low cost preparation method. Nanocrystallisation of the organic phase is realised through the control of the coupling between nucleation, particle growth and matrix polymerisation. We have investigated the main experimental parameters which influence dye aggregation which is favoured when the interactions between the dissolved molecules and the silicate network or the solvent are weak. The volatility of the solvent and the rotation speed are directly related to evaporation of the solvent and thus influence the supersaturation of the organic phase and matrix formation. Our results show that well-defined organic nanocrystals with a narrow size distribution can be grown in gel films. This provides increased stability of the dye as shown for naphthalene. In addition, the optimised nanocrystallisation conditions of the dye are well-reproducible. This generic method can now be extended to other types of organic molecules in order to target other applications such as spectroscopic studies or the development of magnetic materials or chemical sensors.

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