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Influence of processing induced textural effect on aggregation level in CuPc–SiO_2 sonogel composites

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Abstract

Aggregation effects in metallophthalocyanine/SiO_2 composites play an important role in the optical properties of these materials. With the aim to decrease phthalocyanine self-association induced in aqueous solution into the network pores, alternative processing methods for trapping the organic in the matrices have been carried out. Monolithic xerogels have been obtained by three chemically different processing routes, preserving their homogeneity and transparency, even under extremely acid conditions. Micro, meso and non-porous silica xerogels have been obtained, depending on processing method. However, the organic doping highly modifies the textural features of the final composite, increasing the pore volume of composites even in more than 50%. Phthalocyanine aggregation degree has been tested by UV–VIS absorption spectroscopy and correlated to the textural parameters and pore size distribution of the composites. The effect of the textural features on molecular self-association level is evaluated.

1. Introduction

Xerogels have attracted a great interest as matrices to encapsulate organic molecules for a wide variety of applications. Sol–gel process provides a suitable route to obtain transparent stable materials with sufficient quality to use in optical devices [1–3]. The soft processing conditions make possible the incorporation of the dye without thermal damage, leading to transparent solid materials, with improved mechanical properties and stability, more convenient for the use as optical components with different shapes and configurations [1]. Organic molecules can be efficiently trapped into the gel pore network, preserving or even expanding their optical properties due to matrix–dye interactions [4].

These suitable features are improved when the sol–gel reactions are promoted by the use of ultrasonic energy, resulting sonogels with finer and more homogenous texture than those obtained by the classic method, appropriate for optical applications [5].

Metallophthalocyanines (MPc) have attracted strong interest because the large optical nonlinearities associated with their extended delocalizated two dimensional π-electronic systems [6,7]. In

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previous works we have studied the non-linear optical behavior of CuPc–SiO_2 sonoxerogels, and diverse non-linear optical phenomena such as the third harmonic generation (THG) [2], refractive index intensity dependence [3] and reverse saturable absorption (RSA) [8] for optical limiting applications, were evaluated. However, it is well known that these kinds of molecules tend to auto-associate in the pore network, due to the low solubility of phthalocyanine compounds in the common solvents used in the sol–gel route, decreasing their non-linear optical efficiency [9]. In a previous paper [8], we have reported on the aggregation effect on non-linear absorption for a CuPc/silica sonogel composite and pointed about the need to reduce the monomer to aggregate ratio in the material in order to improve the non-linear behavior. With this aim, we have tested different alternative sol–gel processing conditions in order to decrease the dye auto-association in the xerogel structure [10].

As known, the sol–gel processing conditions induce textural changes in the composite [11]. Distribution and anchorage of organic molecules in the network porosity are determined by textural features of the matrix. In this paper, we study the processing induced textural changes in SiO_2 xerogels and CuPc–SiO_2 composites and we evaluate its influence on the distribution of the organic phase in the inorganic network by looking to the optical response.

2. Experimental

Composites obtained from silica xerogels doped with copper phthalocyanine have been studied. In order to evaluate the influence of textural xerogel matrix features on the aggregation state of the dye, three different silica xerogels have been used as matrices. In all the cases, sono-xerogels have been prepared by the sono-gel route using tetramethoxysilane (TMOS) as alkoxide precursor [4]. Hydrolysis and condensation reactions have been carried out in an acid environment and promoted by a high power ultrasound probe (20 kHz, 15 W). For the first type of samples, methanol has been added as solvent in a 3 methanol/TMOS molar ratio, and acidic hydrolysis water, at $pH = 2$, in a molar ratio of 6 H_2O/TMOS (samples called by the code MET). In the second case, methanol is substituted by formamide as drying control chemical additive, as described elsewhere [10], and the resulting composites have been refereed by code FOR. Finally, for the third kind of samples, it is the $pH = 2$ hydrolysis water what is replaced by a 2/3 volume proportion of H_2SO_4/H_2O solution, obtaining the called ACD xerogels.

CuPc/SiO_2 sono-xerogel composites, are obtained adding to the sol, the optically active phase, tetrasulfonated copper phthalocyanine (CuPc), previously dissolved in the hydrolysis water leading to nominal concentrations of 5×10^{-5} M (adding the code 2 to the xerogel code for sample identification) and 10^{-5} M (code 1) in the resulting sol.

In order to study the influence of the matrix on the textural features and optical behavior of the final composites, xerogel matrices and their corresponding CuPc/xerogel composites have been prepared.

Rectangular containers of 5 mm of thickness have been used to gel the samples. In all cases, after three weeks of aging and drying at room temperature, transparent monolithic CuPc–silica xerogels are obtained, which are blue when MET and FOR route is followed, but green in the case of ACD samples. The final thickness is about 3 mm for ACD and FOR xerogels and 2 mm for MET samples. The larger shrinkage in MET samples, gives place to a final volume for dry samples approximately 1/4 of the initial volume in the case of ACD and FOR samples, and 1/10 the initial volume for MET samples. This fact leads to different final phthalocyanine concentration for composites with the same nominal dye proportion but with different chemical processing.

Pore size distribution, specific surface area [12] and porous volume, have been estimated from nitrogen physical adsorption isotherms, on the free surface of samples at the liquid nitrogen temperature. These experiments have been carried out in commercial equipment with an accuracy in the pressure measurement of 0.5% of reading. Samples were previously degassed at 75 °C, in order to remove the liquid from the pores, but preserving the textural features of the composites. Completed adsorption–desorption isotherms have been analysed and pore size distributions have been evaluated from the desorption branches data, using the Dollimore–Heal method [13].

In order to evaluate not only the processing induce textural changes but also the organic phase influence on textural features, nitrogen adsorption experiments have been performed on the xerogel matrices as well as on composites.

Chemical processing conditions effects on phthalocyanine aggregation have been evaluated from UV–VIS absorption spectra.

3. Results

Adsorption–desorption isotherms for different processed matrices are shown in Fig. 1. The curve corresponding to MET matrix can be considered as IUPAC type I isotherm, characteristic of microporous materials, with pore filling at low relative pressure, above which a plateau occurs. However, in the case of FOR matrix, the isotherm corresponds to the IUPAC type IV, presenting a hysteresis loop due to capillary condensation in the mesopores. Almost no adsorption at low relative pressure values is observed for the type ACD matrix, indicating that there is not an important contribution of small pores. For this sample, a small hysteresis loop, at higher relative pressure, appears, due to the presence of mesopores of larger size.

Isotherms obtained for composites (Fig. 2), present in all cases a shape much closer to type IV, showing in all of them, the typical hysteresis loop characteristic of mesoporous solids.

A similar trend is observed from the analysis of textural parameters, shown in Table 1, calculated from adsorption data.

When the *t*-method for microporosity is applied, evidence of micropores is only detected in the case of MET matrix sample, where only a 10% of its surface area is due to the mesopore contribution (Table 1). No evidence of pore size less than 2 nm is found in any other case.

Figs. 3 and 4 show the pore size distributions corresponding to matrices and composites, respectively. In agreement with the information obtained from textural parameters, pore size averages for MET and FOR composites become higher than those corresponding to the matrix. This evolution is particularly evident in the case of

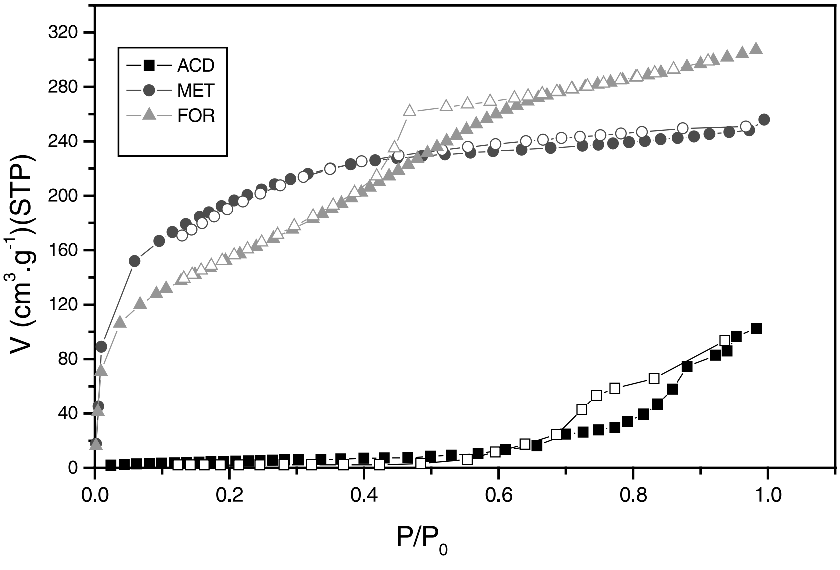

Fig. 1. Adsorption–desorption isotherms for different processed SiO_2 sono-xerogel performed after samples were evacuated at 75 °C.

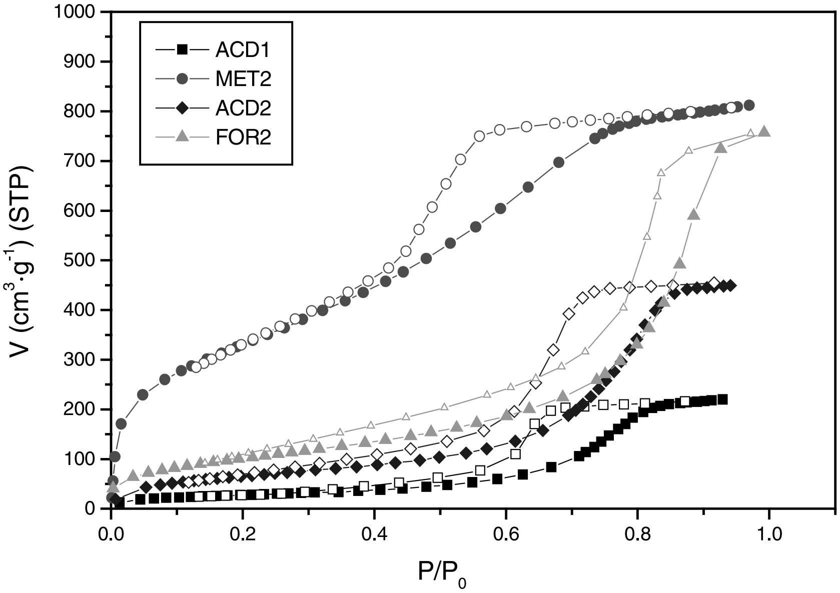

Fig. 2. Adsorption–desorption isotherms for different processed CuPc–SiO_2 composites performed after samples were evacuated at 75 °C.

Table 1
Textural parameters, obtained from nitrogen adsorption isotherms, for samples with different processing and different CuPc concentrations

Sample	Specific surface ($m^2\ g^{-1}$)	Pore volume ($cm^3\ g^{-1}$)	Micropore volume ($cm^3\ g^{-1}$)	Mesopore specific surface ($m^2\ g^{-1}$)
ACD	20.4 ± 0.1	0.158 ± 1E−3	–	20.4 ± 0.1
MET	686 ± 3	0.382 ± 2E−3	0.310 ± 2E−3	68.3 ± 0.3
FOR	415 ± 2	0.565 ± 3E−3	–	415 ± 2
ACD1	102.2 ± 0.5	0.353 ± 2E−3	–	102.2 ± 0.5
MET2	1200 ± 6	1.261 ± 6E−3	–	1200 ± 6
FOR2	373 ± 2	1.112 ± 6E−3	–	373 ± 2
ACD2	248 ± 1	0.702 ± 4E−3	–	248 ± 1

MET sample, where the microporous matrix becomes mesoporous when is doped. Different behaviour is found in type ACD samples in which the low porosity texture with the big pores, found in the matrix, changes to a typical mesopore distribution in samples with phthalocyanine.

In order to find a correlation between the dye aggregation level and the composite textural characteristics, Fig. 5 shows the UV–VIS absorption spectra of different samples, as well as the one for the CuPc in H_2SO_4 solution, used as reference. In all cases, the composite spectra show a blue shifted and broader structure for Q band than the spectrum corresponding to the reference in solution [10], pointing out the presence of aggregate species. The same profile, with a maximum at 692 nm and a higher intensity peak, characteristic of aggregated species, around 614 nm appears for samples MET and FOR. This clearly split Q band does not appear in the case of ACD composite, showing a broad band, typical of a wide dispersion of species, centred at 665 nm.

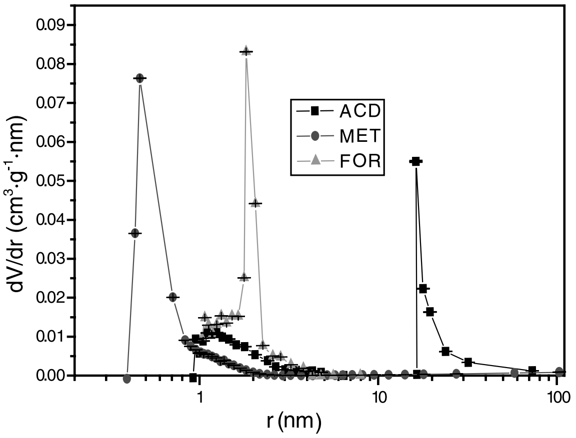

Fig. 3. Pore size distributions obtained from the desorption branch of isotherms plotted in Fig. 1.

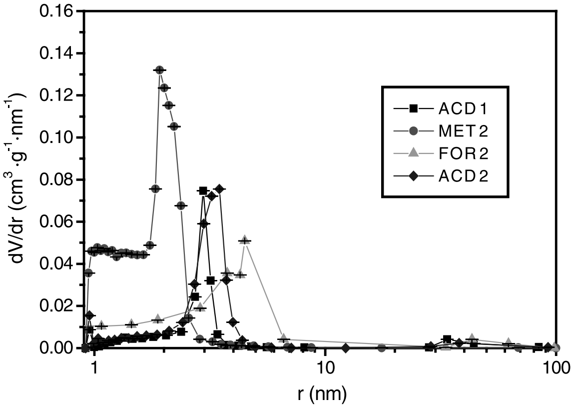

Fig. 4. Pore size distributions obtained from the desorption branch of isotherms plotted in Fig. 2.

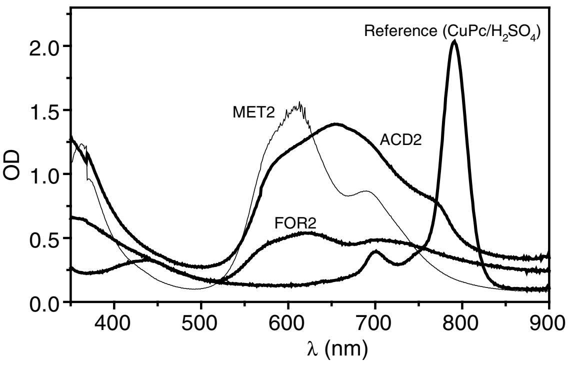

Fig. 5. UV–VIS absorption spectra for CuPc–SiO_2 composites with different chemical processing.

4. Discussion

Results obtained from Fig. 1 points out the possibility to obtain silica xerogels with a wide variety of textural features by changing, slightly, the composition of the precursor sol. In fact, a microporous material is found in the case of MET sample, mesoporous for xerogel FOR, and even almost non-porous when the xerogel is prepared under extremely acidic conditions (ACD matrix). Pore size distributions plotted in Fig. 3, are in agreement with this information obtained from the analysis of isotherms. Sample MET shows a distribution characteristic of microporous materials, with a maximum at size lower than 2 nm. Pore size average is higher, above 4 nm, in the case of FOR sample and only pores of bigger size are found for ACD matrix, that is almost non-porous in the range of micro and mesoporosity. This behaviour, which points out the noticeable influence of processing conditions on the textural features of the final xerogel, is in agreement with the textural parameters in Table 1, showing surface values of only 20 $m^2\,g^{-1}$ for ACD sample, 415 $m^2\,g^{-1}$ in the case of FOR matrix and 686 $m^2\,g^{-1}$ for the xerogel with the smaller pore size average (MET sample).

The initial processing pH value combined to the methanol effect (matrix MET) gives place to the formation of micropores, due to the mechanisms involve in the network formation [14]. In this case, the acidic catalysis promotes the hydrolysis but not the polycondensation and, consequently, the hydrolysis is rather completed before condensation starts, leading to a network with small pore size. When methanol is substituted by formamide, an increase in the pore size average takes place, due to its influence in the polycondensation rate [15,16].

The extremely acid reaction conditions (ACD samples), drastically modify the condensation mechanism. Hydrolysis reaction is strongly catalysed and, consequently, polycondensation occurs between clusters of especially small size provoking the network formation in absence of fine porosity.

The situation is obviously different when the xerogel is doped with the organic phase (Figs. 2 and 4). The presence of dye aggregates obliges the xerogel network to form around this organic phase. Under these conditions, silica cluster are able to grow up further before cluster–cluster aggregation occurs, giving place to an increase of the pore size average. Due to this phenomenon, MET sample becomes mesoporous when doped, and in the case of FOR type sample, the doping process induces an increase in the pore size average from 4 to 8–10 nm. In general, for these two kind of samples, the textural characteristics are mainly dominated by the processing conditions. Nevertheless, a different behaviour is observed in ACD samples, for which the matrix isotherm corresponds to a non-porous material, with a very low pore volume distributed in pores of size close to 50 nm. For these samples, a clear increase in the pore volume as well as a decrease of the pore size average is pointed out when organic phase is encapsulated in the xerogel. As has been discussed, for the matrix, the extremely acid processing parameters promote the network formation between especially small size clusters, due to the network collapses under these conditions, avoiding the micro and mesopores formation. When ACD sample is doped with the organic dye, the presence of this phase avoids this collapse, inducing the formation of mesopores, due to the clusters are able to increase the size around the organic aggregates. The result, composite ACD1, is a mesoporous material (Fig. 2) with a narrow pore size distribution centred around 6 nm (Fig. 4). When organic phase concentration increases, composite ACD2, the same phenomenon originated by the organic phase effect, described for MET and FOR samples occurs, leading to a mesoporous solid with a smoothly higher pore size average than ACD1 composite. In this case, the main change takes place when the matrix is doped and there are not important differences between pore size distributions of composites with different organic phase concentration.

As expected, smaller surface area (Table 1) values are found for type ACD samples, especially in the case of the ACD matrix, because there is not a great contribution of mesopores to the specific surface. When this sample is doped, surface area increases, due to the formation of mesopores induced by the organic phase effect in the network formation. These values drastically increase for MET samples in which the proportion of small pores is considerably more important.

The splitter Q band for MET and FOR composites indicates a larger ratio of aggregated species to monomer. However, the broader and less intense band in FOR than MET can be interpreted as a spreading of associate species for FOR samples regarding to MET composites. The lower pore size average for MET composites can contribute to limit the self-association of molecule into the network porosity. In the case of ACD sample the band is quite broad compared to the one for the reference but, however, there is a shoulder at 760 nm indicating the contribution of monomer species.

The combination of extremely acid processing parameters together with the organic doping effect, leads to composites with the narrowest pore size distribution, contributing to the control of dye aggregate size. This narrow distribution could be determined by a smaller organic cluster size in samples ACD, due to the lower aggregation level reached in these types of materials.

Results reveal an influence of processing conditions and textural characteristics of the xerogel, on the organic phase aggregation state in the composite. However, the textural features of composite strongly depend on the organic doping effect. For this reason, it is not always possible to design the texture of the final composite based on the characteristics of matrix since these are modified by the trapped phase influence.

5. Conclusions

Textural characterisation of CuPc–silica composite, obtained by three different procedures, has been carried out and correlated with the organic phase aggregation state in the matrix network. Micro, with pore size average less than 1 nm, meso, with pore size above 4 nm, and non-porous silica xerogels are obtained by changing only the processing parameters. Textural features are strongly modified when the organic phase is encapsulated into the xerogel. In the case of samples MET and FOR, the network growing around the organic aggregates provokes an enlargement of the pore size average until reaching diameters of 4 and 9 nm respectively. Under extremely acidic processing conditions, the initially almost nonporous material increases its pore volume in a 50% becoming mesoporous due to this organic phase influence. Processing conditions and concentrations of initial precursors have an influence on material texture and aggregation state of organic phase. However, the organic doping highly modifies the textural features of the final composite.

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