

# Use of Time-Resolved Fluorescence Analysis to Assess Molecular Mobility and Ionic Conductivity in Nanocomposite Organic-Inorganic Gels

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This work is a short review of studies on nanocomposite organic-inorganic gels by stretched-exponential analysis of fluorescence decay profiles. Emphasis is given to the conditions which allow maximum probe mobility and minimum confinement conditions with the aim to assess ionic conductivity in these materials and with the purpose to employ them with dye-sensitized photoelectrochemical solar cells and other analogous systems.

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**KEY WORDS:** Nanocomposite gels; fluorescence; molecular mobility; ionic conductivity.

## INTRODUCTION

Nanocomposite organic-inorganic (NOI) gels consist of two interpenetrating subphases, one organic and one inorganic mixed in the nanoscale. The inorganic subphase (ISP) is made of an inorganic network, typically SiO<sub>2</sub> or TiO<sub>2</sub>, synthesized by the sol-gel route. The organic subphase (OSP) can be made out of a large variety of organic substances or combination of organic substances. A literature review shows that the number and variety of such combinations already composes a vast list [1–13]. It is nevertheless a matter of fact that a few surfactants and polyether chains are most popular choices for the OSP composition [1–3,7,10]. The two subphases can be a simple mixture or they can be covalently bound by choosing the appropriate sol-gel precursors. Both possibilities are applicable, in accordance with functionality, availability and chemical synthesis possibilities.

NOI gels can be studied by various spectroscopic or imaging techniques. Microscopy is applicable in the case where sufficient contrast exists between clusters of inor-

ganic and organic subphases. However, because of their mixture in the lower nanoscale such a contrast is only available in some limited convenient cases. X-ray diffraction techniques are also limited to the presence of short or long range order. In the majority of cases, both microscopy and X-rays are useless. Therefore, study of NOI gels mainly relies on spectroscopy. In this respect, fluorescence probing has demonstrated a vast capacity for the study of NOI gels, both in terms of structure and dynamics, both in terms of mobility and structural evolution. The present work, which is a short review of our recent studies in this domain, focuses on molecular mobility and ionic conductivity in NOI gels, studied by time-resolved fluorescence quenching analysis. As an application, a brief description is also presented of Dye-sensitized quasi-Solid-state Solar Cells (DSSC), which constitute an alternative solution for the photovoltaic conversion of solar energy and which take major advantage of NOI materials [14–16].

## THE SOL-GEL PROCESS: PAST AND PRESENT

Sol-gel is a chemical process which starts with a mixture of reagents making a transparent sol and ends up to a solid gel and finally, after slow evaporation of volatile

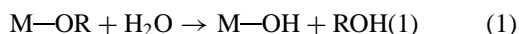
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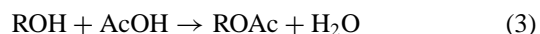
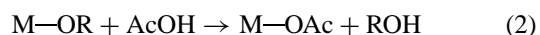
components, to a xerogel. Even though the term has a more general sense, it is usually employed to designate the hydrolysis of a metal alkoxide (including silicon alkoxides) and the subsequent inorganic polymerization (condensation) that leads to formation of the corresponding oxide [17,18]. The whole process is carried out at ambient or slightly elevated temperature. The most extensively used reagents are silicon alkoxides while compounds of several transition metals, such as Ti, Sn, Zn or V, are also very popular. One of the principal applications of the sol-gel process is the fabrication of transparent amorphous oxides doped with functional organic groups. Since sol-gel doping is done at ambient conditions or at slightly elevated temperatures, organic dopants can be preserved both in terms of composition and functionality. Thus silica has been doped with a great variety of organic substances ranging from laser dyes to proteins and other functional macromolecules [3,5,8,9,11]. It was, however, soon made clear that pure sol-gel matrices (in most cases, silica matrices) have serious drawbacks. The solubility of most organic substances, especially, hydrophobic ones, is limited in pure silica, causing migration and aggregation and subsequent decrease of functionality. This is one main reason that research has turned to nanocomposite materials, made of two subphases mixed in the nanoscale, one organic and one inorganic. The inorganic subphase is the oxide network. The organic subphase aids solubilization and dispersion of functional dopants while in some cases the functional dopant itself constitutes the organic subphase. A second main reason for seeking for nanocomposite materials is templating of mesoporous structures. This method, which constitutes nowadays a vast field in materials research, uses organic mesophases in nanocomposite materials as templates to build porosity in oxide matrices. When the template is removed, either by calcination or by using appropriate solvents, it leaves behind a mesoporous structure, which can be designed to have a high degree of order [19–23].

The chemistry involved in the sol-gel process can be summarized by the following reaction schemes. A typical and best known sol-gel process is based on hydrolysis of an alkoxide [17], according to the reaction



where M is Si, or Ti or another metal and R is a short aliphatic group (e.g., methyl, ethyl, isopropyl, etc.). The highly reactive M—OH thus created can polymerize (M—O—M) and lead to gelation only if it is kept in suspension. However, hydrolysis is exothermic and violent, particularly, in the case of transition metal alkoxides and usually it leads to undesirable routes, such as precipitation of particles of large size and uncontrollable shape

and, generally to poor quality gels. It is then necessary to seek ways to make this process slow and controllable. There are several alternatives which have been proposed, including precipitant peptization [24], use of surfactant or polymer templates [25], reverse micelles [26], etc. Recent works choose to synthesize oxides by slow water intake from the environment and from the water attached to the reagents in the precursor sol [27,28]. However, best so far results have been obtained by introducing an organic acid in the sol [29,30], typically acetic acid, other organic acids being also applicable. Scientists working with sol-gel materials often feel that sol-gel process is a skillful art rather than exact science. This always happens when many parameters intervene in a process and this is actually what AcOH brings about. This is seen in the following reactions, demonstrated in the past by spectroscopic techniques [15,29–31]:



(In reactions (2)–(5), as well as in the above reaction (1), only one of several reacting alkoxy groups is taken into account, for reasons of simplicity). Reactions (1)–(5) show that the end product of the sol-gel process, that is M—O—M, can be obtained by a colorful choice of chemical routes. Reaction (2), followed by (5) can lead to M—O—M, while water released through esterification reaction (3) can yield oxide by the hydrolysis route. When ethanol is introduced in the sol, which is a common practice in many works, even more water can be released by direct EtOH—AcOH esterification reaction [30,31]. Furthermore, intermediate M—OAc ester or M—O—M oligomers may create entities which offer polymorphism to the sol-gel evolution. Thus the presence of a self-organizing agent, e.g. a surfactant, plays a crucial role in organizing the structure of the material and in creating well defined and reproducible nanophases. Slow water release, organic acid solvolysis and surfactant organization are then the key factors that dictate the structure and the quality of a NOI gel. In the present work we make reference to gels produced by exploiting various slow water release factors so that NOI gels are produced in a controlled and reproducible manner.

## FLUORESCENCE STUDIES

The present work focuses, as already said, at molecular mobility in NOI gels. One almost ideal method to study

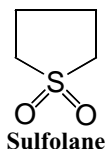
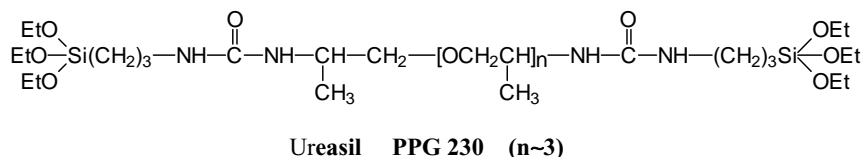


Fig. 1. Chemical structure of ureasil PPG-230 and sulfolane.

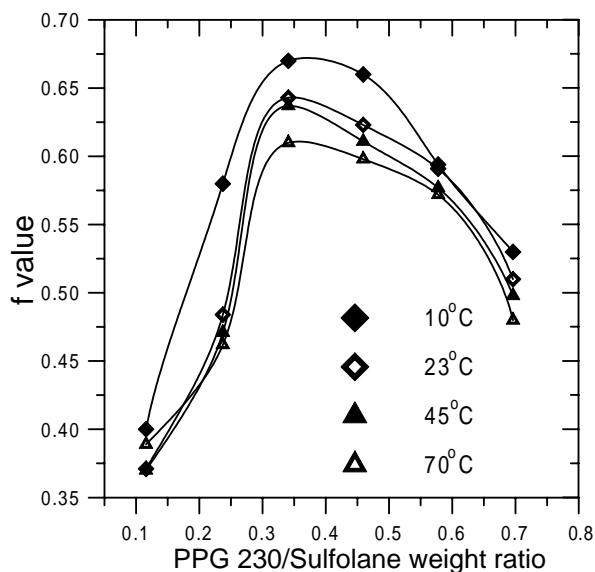
molecular mobility, albeit indirect, is Time-resolved (TR) fluorescence quenching analysis. As it has been previously shown [32], TR analysis in complex nanophase systems is best made with stretched exponentials given by the following fluorescence decay model:

$$I(t) = I_0 \exp(-t/\tau_0) \exp[-C_1(t/\tau_0)^f + C_2(t/\tau_0)^{2f}] \quad (6)$$

where  $0 < f < 1$ ,  $C_1$  and  $C_2$  are fitted parameters and  $\tau_0$  is the decay time of the fluorophore in the absence of quencher.  $f$  is larger in less restricted domains and it theoretically takes values  $\geq 0.67$  at and above the percolation threshold in clusters possessing fractal (self-similar) geometry [32]. Most of these nanostructured materials are practically fractals so that the above theoretical value is a good reference point. By fitting Eq. (6) to the fluorescence decay profile, the value of  $f$  can be calculated, offering information on the studied gel. The procedure is as follows. The reagents used to make the precursor sol in the sol-gel process are mixed together with the fluorescent and the quencher molecules. To make bulk gels, the sol is placed in a plastic container and is left to slowly dry until it becomes solid gel. The resulting geometry is defined by the geometry of the template (container). Also a film can be deposited by dipping or casting. In our case, films used for fluorescence analysis were deposited on glass slides by dipping. For DC conductivity measurements films were obtained by sandwiching sol between two ITO or  $\text{SnO}_2:\text{F}$  electrodes. In both cases films were left to dry in air [14–16]. When the gel is formed, both fluorophore and quencher find themselves solubilized in the organic subphase (OSP) and they choose domains that fit their polarity. For example, when pyrene and coumarine-153 (C153), a typical donor-acceptor Foerster-energy-transfer couple [7,33], are solubilized in silica/cetyltrimethylammonium gels [7],

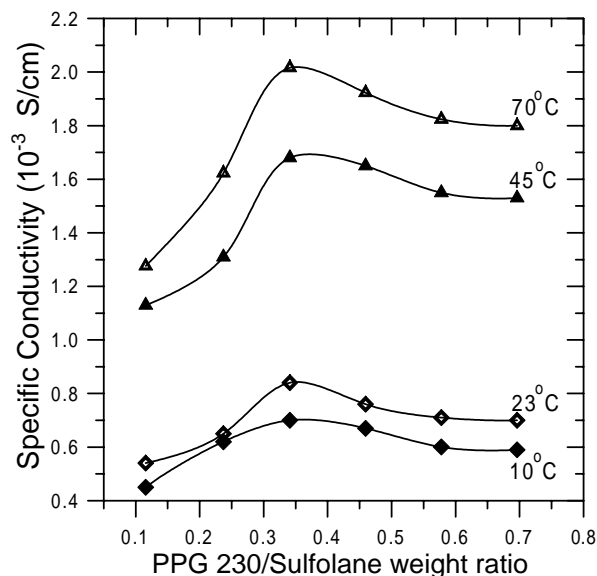
they probe the hydrophobic surfactant domain. When the charged  $\text{Ru}(\text{bpy})_3^{2+}/\text{MV}^{2+}$  luminophore/quencher couple is incorporated in the same gels, it is confined and probes the polar silica surfactant interface [7]. The confinement of the charged couple directly reflects on the value of  $f$  which is smaller in the case of the charged than in the case of the hydrophobic couple [7]. In other words, the value of  $f$ , obtained by fitting Eq. (6) to the fluorescence/luminescence decay profile, is an information useful to map the environment where probe and quencher are solubilized.

With the above information in mind, let us examine a case of Ureasil NOI gels that we have been using as electrolyte supports in DSSC cells [15]. Ureasil [10] precursors consist of a polyether chain end-capped by two triethoxysilane groups bonded by urea bridges (hence ureasil). For example, Ureasil PPG230 contains a chain of three propyleneoxide groups [10] (cf. Fig. 1). Films were made by using NOI gels synthesized in the presence of AcOH, i.e. according to reactions (2)–(5). By analyzing the luminescence decay profiles of pyrene in the presence of C153 with Eq. (6),  $f$  was found equal to 0.35. This value is very small and far below the theoretical percolation threshold of 0.67 introduced in the previous paragraph. This means that gels made of pure ureasil PPG230 do not provide a percolating OSP. Subsequently, such gels are not good to be employed as ionic conductors. Indeed, ureasil PPG230 gels with incorporated ions gave very poor conductivity results. It soon became clear that in order to improve conductivity, it is necessary to introduce a solvent, which mixes with the OSP increasing its volume fraction. We have tried a large number of solvents and studied percolation conditions by analyzing the fluorescence decay profiles of pyrene in the presence of C153, according to Eq. (6). Figure 2 presents  $f$  values found for gels made of PPG230 and sulfolane at four different temperatures



**Fig. 2.** Non-integer exponent  $f$  values at different temperatures vs. gel composition: Values of  $f$  found by analysis of fluorescence decay profiles of pyrene in the presence of coumarin-153. Pyrene concentration 1 mM. Coumarin-153 concentration varied between 2–5 mM. Measurements were made on films obtained by dip-coating sol on glass slides.

(for chemical structure of sulfolane see Fig. 1). The results are interesting and rather surprising. Similar behavior was found with other solvents, e.g. propylene carbonate, acetonitrile pyridine, etc. One would expect that molecular confinement would continuously decrease by increasing solvent content and this should reflect on increasing values of  $f$ .  $f$  did increase but then it achieved a rather sharp maximum at a well defined PPG230/solvent ratio, not depending on temperature. Even more surprising was the fact that  $f$  values, i.e. molecular displacement dimension, decreased with increasing temperature, even though the opposite was expected. It is obvious that even though NOI gels are solid materials they can undergo changes of their physical state under the influence of external parameters, such as temperature. In this respect it will be interesting to examine these gels also by other physical techniques and this work is under way in our laboratory. Figure 2 tells us that the ideal PPG230/sulfolane ratio for lowest molecular confinement is around 0.3. This conclusion was justified by DC conductivity data presented in Fig. 3. Again, maximum conductivity was obtained at the PPG230/sulfolane ratio of 0.3. Conductivity data were obtained by incorporating KI and  $I_2$  in the gel, which produce the  $I_3^-/I^-$  redox couple used in DSSC cells [14–16]. The conductivity values increased, as expected, with temperature. The comparison of the data of Figs. 2 and 3, gives in a rather clear manner the extent of representation of molecular mobility by the exponent  $f$  of Eq. (6).  $f$  is a



**Fig. 3.** Dark DC conductivity values at various temperatures vs. gel composition. Measurements were made on films sandwiched between two  $SnO_2:F$  electrodes. Sol contained 0,5 M KI and 0.05 M  $I_2$ .

geometrical parameter mapping the structure of the OSP which is built up of individual communicating clusters.  $f$  value is proportional to the (fractal) dimension of the clusters as a whole. Increase or decrease of  $f$  means increase or decrease of the effective dimensionality of the domain (the OSP) probed by the fluorophore quencher couple. Existence of an extremum in dimensionality means that too much of solvent makes it hard to be properly mixed and dispersed within the OSP. Too little of solvent does not provide enough material to make a percolating OSP. The fluorescence analysis then provides the means to estimate the right proportion of components for an optimized system. Finally, the fact that  $f$  decreases with increasing temperature means that the ureasil backbone reorganizes itself adopting a lower-dimension geometry at higher temperature. All these matters are subjects of further study in our laboratory.

Conductivity measurements combined with fluorescence analysis data has helped us develop gel electrolytes that can be employed with DSSC for the photovoltaic conversion of solar energy. These cells are made of nanocomposite materials sandwiched between fluorine-doped tin oxide transparent electrodes  $SnO_2:F$  [14–16]. On the one  $SnO_2:F$  electrode, a thin nanocrystalline titania film is deposited by dip-coating a NOI gel [26] and then calcinating at 500°C. Then a dye sensitizer is adsorbed and bound on titania, in order to absorb visible light. Finally a  $I_3^-/I^-$  redox electrolyte supported in a NOI gel (e.g. ureasil+solvent, see above) is squeezed between

the titania/dye electrode and a second  $\text{SnO}_2\text{:F}$  electrode [14–16]. Satisfactory external conversion efficiencies of more than 5% have been recently obtained by using different types of NOI gel electrolytes [15,16].

## CONCLUSION

Time-resolved fluorescence analysis by stretched exponentials is a simple and sensitive tool that can be used to determine percolation conditions in a nanocomposite organic-inorganic gel. The procedure consists of incorporation of a fluorophore/quencher couple into the gel and of analysis of the fluorescence decay profiles by the model of stretched exponentials of Eq. (6). Such analysis provides the non-integer exponent  $f$ , a quantity which is proportional to the effective dimensionality of the host domain, which marks the conditions for attaining an optimized system.

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