

Effect of the condensation of hybrid organic–inorganic sol–gel materials on the optical properties of tripan blue



Craig Hicks, Muhammad Morshed, Garrett Melia, Killian Barton, Brendan Duffy, Mohamed Oubaha*

Centre for Research on Engineering Surface Technology (CREST), FOCAS Institute, Dublin Institute of Technology, 13 Camden Row, Dublin 8, Ireland

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ABSTRACT

The work reported in this paper highlights the effect of sol–gel structures on the optical properties of a typical organic dye (Trypan Blue, TB). Three transition-metal-based hybrid sol–gel materials with different structures and morphologies were developed and characterised by TEM. The optical properties of TB were investigated by incorporating it in the different sol–gel materials and the UV–Visible spectra recorded in both liquid and solid state, in thin-coatings cured at temperatures in the range 100–150 °C. These studies revealed two relevant results. First, the sol–gel morphology plays a critical role in the optical properties of the dye. The effect of the sol–gel host matrix on the optical properties of the dye is attributed to the steric hindrance of the nanostructures, themselves intimately dependant on the reactivity of the transition metal. For instance, the less condensed system showed the highest reactivity with the dye, while the more condensed system exhibited limited interaction with the dye, symbolised by a significant change or quasi-unchanged UV–Visible spectra, respectively. It is also shown that the increase of the condensation degree of the sol–gel coatings by heat-curing can dramatically alter the optical properties of the dye especially for the most condensed sol–gel systems. This has been attributed to proximity effects enabled by the further increase of the materials densities.

The results reported here aim to provide a better understanding of how material formulations can influence the optical properties of organic dyes and suggest that the structure of the host matrix along with the applied curing process have to be fully considered and assessed in the choice of organic dyes for a given application.

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1. Introduction

Over the past decade, organic dyes have found applications in a number of scientific fields and industries including, colorants for plastics [1], inks [2], paints [3] and cosmetics [4], optical and lasers for telecommunications [5], sensing for medical diagnostic [6] and environmental monitoring [7] and electronics [8]. For most of these applications the essential objective of using organic dyes is to employ their intrinsic physical properties to provide advances in aesthetic or enable to highlight a physicochemical event that may occur due to an external stimulation.

In most cases, the dyes are dispersed in a liquid matrix, usually a polymer or a glass, and the resulting optical properties of the final materials associated to the dye behaviour. This approach is true when the role of the host material is limited to the dispersion and homogenisation of the dye within it. It is however more complex when interaction of both systems take place at the molecular level as this can result in the modification of the intrinsic physical

properties of the dyes, the consequence of which could be a more or less significant alteration of the final properties of the system. It is thus essential to identify the effects of the possible physico-chemical mechanisms, including both chemical reactions and degree of entrapment in a host matrix that can take place between both systems, which can alter the optical properties of the materials. To our knowledge, no study has so far aimed to highlight these phenomena.

The objective of this paper is to contribute in addressing this gap of knowledge and possibly initiate a number of fundamental studies in the field of dyes. For this, three hybrid sol–gel materials with different condensation capabilities, resulting in dramatically different structures and morphologies, are employed to highlight the effect of the structure of the host materials on the physico-chemical properties of a selected organic dye, namely Trypan Blue (TB). The strategy to control the structure of sol–gel systems used in this work consists of controlling the degree of chelation of the employed transition metal. Similar studies outlining the effect of the ligand on the condensation of metal alkoxides have been performed before in pure inorganic alkoxide precursors

* Corresponding author.

[9,10]. However, our study differs in the nature of the employed precursors and in the development of dual sol–gel systems, containing both transition metal and organosilicate precursors. The structure of the host matrices are characterised by transmission electron microscopy (TEM). The optical properties of the dye are followed by UV–Visible absorption in liquid and solid states, as coatings deposited on glass substrates. The effect of the curing temperature of the fabricated coatings is also investigated and the obtained results are explained by correlating the structures and reactivity of the host materials and their interactions with the dye. Understanding of these parameters will help in the design of dyes with specific molecular structures targeting innovative optical materials for a wide range of applications.

2. Experimental

2.1. Sol–gel synthesis

The synthesis of the sol–gel matrix involved the formation of a stable and homogeneous sol obtained from the mixture of an organically modified silicate, the hybrid precursor 3-methacryloxy propyltrimethoxysilane (MAPTMS, $C_{10}H_{20}O_5Si$, Assay 99% in methanol, Aldrich), zirconium (IV) n-propoxide (ZPO, $C_{12}H_{28}O_4Zr$, Assay 70% in propanol, Aldrich), and methacrylic acid as ligand (MAAH, $C_4H_6O_2$, Assay > 98%, Aldrich). As sketched in Fig. 1, the synthesis involves a three-step process. MAPTMS is initially pre-hydrolysed by employing a HNO_3 aqueous solution (0.1 M). At the same time, ZPO is chelated using MAAH. After 45 min of reaction both solutions are incorporated together. A release of heat is observed suggesting the formation of irreversible and fully stable chemical bonds. Following another 45 min of reaction, a second hydrolysis is performed to lead the hydrolysis degree to 50% of the total sol–gel reactive groups and allow the continuation of the polycondensation reactions. This hydrolysis degree is found to be very adequate as the obtained solutions exhibit viscosities comprised between those of water and light oils, thus allowing the formation of homogenous and transparent coatings with thicknesses in the micron scale range. In this study the molar ratio of the precursors have been altered in order to achieve nanomaterials with different morphologies and subsequently assess the influence of these morphologies on the UV–Visible absorption of a selected organic dye. To this end, the relative proportion of ZPO against MAAH was altered, while keeping the amount of MAPTMS constant. The molar contents of the three developed formulations are: 10:2.5:2.5 (material A), 10:2.5:0.625 (material B) and 10:2.5:0 (material C).

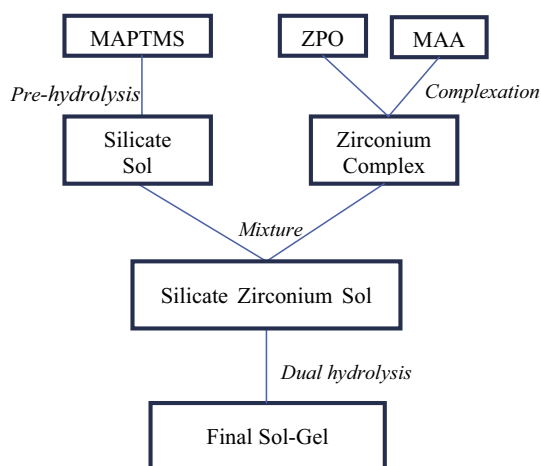


Fig. 1. Flow chart for the preparation of the hybrid sol–gel materials.

Trypan blue (3,3'-[(3,3'-dimethyl-4,4'-biphenyl)yl]bis(azo)] bis(5-amino-4-hydroxy-2,7-naphthalenedisulfonic acid) is the selected dye in this study (Fig. 2). It is a symmetrical molecule containing amino, hydroxyl and sulfoxide groups grafted onto a naphthalene group itself linked to a benzyl group through an azo function, which was added as 1% mol. against the transition metal at the end of the sol–gel synthesis.

2.2. Characterisation techniques

The UV–Visible absorption spectra (200–800 nm) were recorded using a Cary Varian 50 scan spectrophotometer with a resolution of 4 cm^{-1} . The scan speed was 600 nm/min. Liquid samples were analysed using polypropylene cuvettes. Measurements of solid samples were recorded using thin coatings deposited by spin-coating of the different sol–gel solutions onto quartz slides and thermally stabilized at different temperature ranging from 100 to 150 °C for 1 h.

FTIR spectra of all coatings cured at the three different temperatures of interest were recorded using a Perkin Elmer GX instrument operating in the ATR mode within the $600\text{--}4000\text{ cm}^{-1}$.

Transmission electron microscopy (TEM) was performed on a TECNAI G2 20 Twin electron microscope in bright field mode at 200 kV. The sections were prepared using a Leica EM UC6 ultramicrotome cutter with a cryo-chamber (EM FC6).

3. Results and discussion

3.1. TEM analysis of hybrid sol–gels

Fig. 3 shows the TEM images of the three hybrid sol–gel materials. A progressive increase of the particle size can be observed as the degree of chelation of the zirconium atom is decreased. For material A, most of the particles are in the nanometre scale ($<10\text{ nm}$). The TEM image of material B indicates that it is relatively homogeneous and dense with a particle size varying from 10 to 200 nm. However, the particle size of material C is in the micron range with an apparent gradual decrease in the density from the centre to the surface, as observed by the change in the contrast of the image of the particle.

These observations suggest that the formulation of these three materials has a direct impact on the reactivity of the hybrid systems to the sol–gel hydrolysis and condensation reactions, as well as on the subsequent structure and morphology of the formed particles. In fact, the main difference between these materials resides in the degree of chelation of the zirconium atom, the role of which has been identified in previous studies in catalysing the formation of siloxane bonds and participating to the formation of the inorganic backbone of the material [11–13]. In material A, the ligand is added in a stoichiometric ratio against the zirconium precursor, resulting in preventing 50% of its propoxide groups to undergo hydrolysis and further participate to the condensation reactions. In material B, only 25% of the propoxide groups are chelated, suggesting that 75% of the remaining groups are free to undergo hydrolysis and subsequently contribute to the formation of the

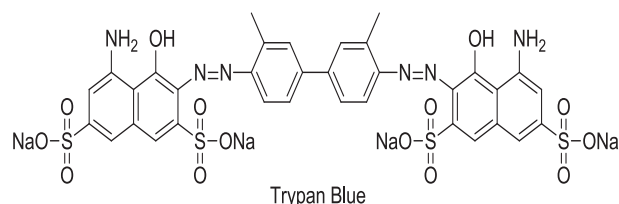


Fig. 2. Chemical structure of tripan blue.

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