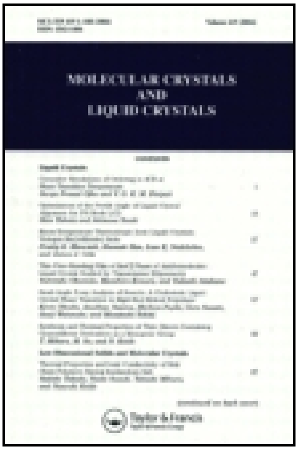

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Preliminary Results for DNA-Surfactant Ni(II) Complex Structures Inclusions into Hybrid Organic–Inorganic Nano-Composites

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The supramolecular structure Ni(II) complex compound-DNA base-surfactant encapsulated within hybrid organic–inorganic silica nano-matrix has been obtained in a highly ordered form based on template synthesis of controlled sol-gel method. Some pre-defined properties of nano-matrix which depends on collective steric properties of supramolecular structure containing complex compound-DNA-surfactant according to the identification and using of an adequate surfactant for specific process of complex compound-DNA bonding have been investigated. The principal application deals at including supramolecular structure containing complex compound-DNA-surfactant in a silica nano-matrix, in order to obtain an intelligent material with optoelectronic properties.

Keywords: enhanced flurescence; hybrid organic–inorganic siloxane; Ni(II) – DNA nucleobases – surfactant interaction; surfactant ordering effect

INTRODUCTION

Self-assembled surfactant-templated synthesis has been considered a versatile attractive technique not only for revolutionary mesoporous materials but with an increasing interest in the last decade in bio-encapsulation technology and especially for drug delivery study [1–5], due to both their physical attributes and their simple bottom-up solution phase self-assembly process, which allows for a massively

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parallel synthesis. This synthesis fitted very well with the sol-gel process and its broad range of physical attributes and possible applications, especially in the field of biomaterials and marks this technology as one of the most promising field of contemporary material science [6–8].

For the purpose of biocompatibility and versatility of methodology for biological applications the hybrid organic–inorganic synthesis based on sol-gel technique is very promising. Silica based carrier is not a food source for micro-organisms, is not toxic and it is biologically inert. The sol-gel derived hybrid organo-siloxanes process is very close as compatibility to the bio-mineralization processes in the living organisms. Bio-mineralization occurs in water, at room temperature under mild conditions (pH neutral etc) at which proteins or cells are active. The sol-gel process can be easily adapted to bio-molecules and bio-encapsulation can occur in many steps, removing all possible denaturative interactions (solvents, high temperature, pH). Physically trapped biomolecules within hybride organo-siloxane colloids will have enough protective space and still undergo the necessary conformational changes for binding and release of substrates. The great advantage of sol-gel encapsulation within colloidal route is represented by the conservative "protective free-space" maintenance, into which the biomolecule can exert its activity by comparison with those of nanopore controlled motions limited by steric and field effects.

This research study aims at using some oxidic nano-matrices special adapted as organizing host for the complex compound-DNA-surfactant system and with the controlling possibilities for hosted supramolecular structure through steric or field coordination effects. This application aims at including supramolecular structure containing complex compound-DNA-surfactant in a silica nano-matrix, in order to obtain an intelligent material with possible optoelectronic properties.

MATERIAL AND METHODS

A derivative polymeric sol-gel tool, using as template molecules new surfactants able to obtain controlled nanopores and nanochannels systems over 15 nm in diameter has been used. The method and reagents are published elswhere. This value was selected from the free motion diameter resulted for DNA-surfactant-metallic complex system so that to be exceeded the electronic and geometric interactive area, as in the cross section double stranded DNA molecule free diameter is bellow 2.4 nm. Methodology of synthesis is based on a sol-gel polymeric tool, which has been developed and published by authors on several communication [9,10]. Different ligands, such as aceto-acetoxy-ethyl-methacrylate (AAEM) and methacryl-amido-salicylic acid (MASA), both of which presenting a strong chelating part and a highly reactive methacrylate group have been used for silica matrix formation process. The principal silica source was Tetra-Ethyl-Ortho-Silicate (TEOS). Dimethylsiloxane oligomers (linear and cyclic species) cross linked at molecular level have been synthesized.

The exhaustive characterisation results are subject of an ample scientific article under publication.

Complex compounds with square planar geometry [Ni(bpy)(cys)$_2$] where bpy = 2,2′ bipiridine or its 4,4′dimethyl derivative and cys = amino acid cysteine [10] have been used.

FT-IR spectra were recorded with a FT-IR 620 spectrophotometer, (Jasco, Japan) in 4000–400 cm^{-1} domain;

UV-VIS-NIR spectra were recorded with a UV-VIS-NIR spectrophotometer, V570 (Jasco, Japan) with a domain between 200–2000 nm with reflexion device ILN-472.

Scanning Electron Microscopy spectra were registered with a Scanning Electron Microscopy Philips XL30 ESEM.

RESULTS AND DISCUSSION

Comparative study of registered UV-Vis spectra for Ni-complex, sol-gel encapsulated Ni-complex and sol-gel encapsulated Ni-complex-DNA base system shows a significant evolution of structure during the encapsulation process (Fig. 1). Specific metal-to-ligand charge transfer transition UV signal disappeared after sol-gel Ni-complex encapsulation due to the ligand change process with the silica-gel polymeric species. This could be attributed to the new interactions and structural rearrangements of complex after sol-gel inclusion. The addition of DNA – base dramatically change the spectrum in the area of d-d ligand charge transfer interaction, the most probably due to the new electronically interaction offered by DNA – base.

Fluorescence measurement reveals a substantial enhancement of activity after DNA-base inclusion (Fig. 2). These results are sustained by the electronic spectra and attributed to the new electron transfer possibilities induced by spatial rearrangements both in the presence of polymeric matrix structure and DNA – base presence.

Scanning electron microscopy pictures of non thermally treated samples shows a possible micro-metric lattice arrangement with holes around 100 microns due to the presence of siloxanic polymer chains and a completely amorphous structure.

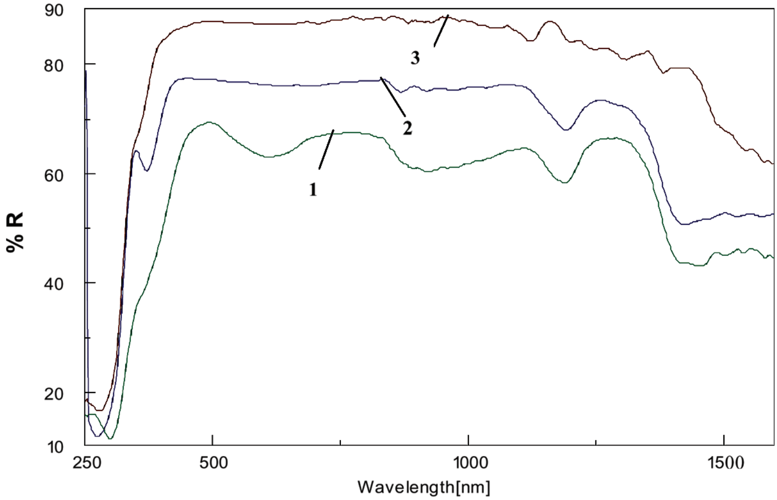

FIGURE 1 Comparative electronic spectra during encapsulation process for: 1. [Ni(bpy)(cys)]; 2. encapsulated Ni-complex-DNA base; 3. encapsulated Ni-complex.

CONCLUSION

The fluorescence activity is substantial enhanced after sol-gel inclusion of Ni metallic complex (Fig. 3-blue line). Important electronic transfer properties are obtained after complex inclusion into the organic-silica nano-matrix. The specific interaction between surfactant and cytosine

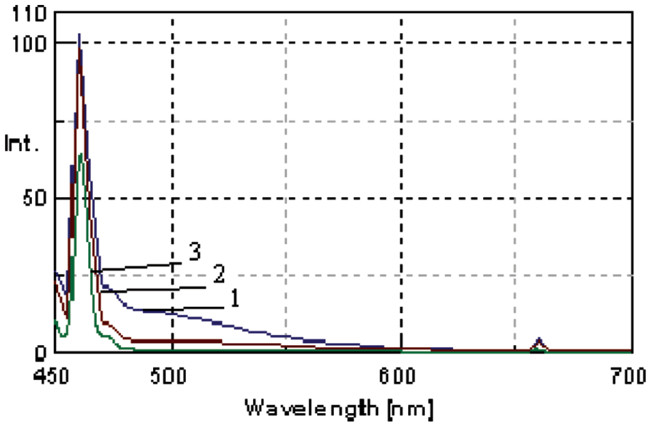

FIGURE 2 Comparative fluorescence spectra during encapsulation process for: 1. [Ni(bpy)(cys)]; 2. encapsulated Ni-complex; 3. encapsulated Ni-complex-DNA base.

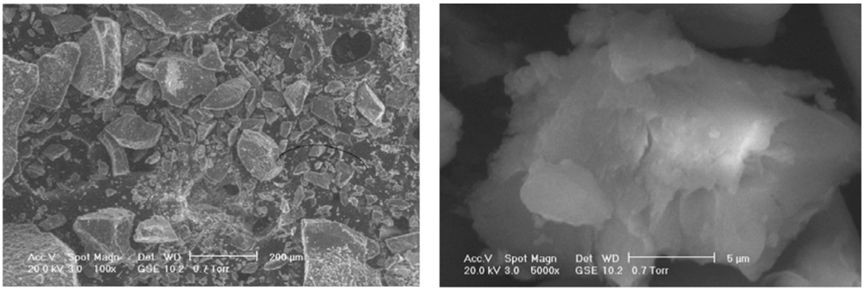

FIGURE 3 SEM picture of DNA-complex-nano precursor shows the surfactant ordering effect and the perfect amorphous state of material at different focusing scale: 200 µm and 5 µm

DNA base is sustained by IR and UV-Vis spectra. The compound obtained presents superior fluorescence properties comparative to simple complex, thus being promising material for optoelectronic applications.

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