Journal of Non-Crystalline Solids 357 (2011) 1716–1723

Contents lists available at ScienceDirect

Journal of Non-Crystalline Solids

journal homepage: www.elsevier.com/locate/jnoncrysol

Vegetal nanoclusters in hybrid silica films prepared by sol-gel spin coating technique

I. Lacatusu, N. Badea, A. Murariu, C. Pirvu, A. Meghea *

University POLITEHNICA of Bucharest, Faculty of Applied Chemistry and Materials Science, Polizu Street No 1, 011061, Bucharest, Romania

ARTICLE INFO

Article history:
Received 5 October 2010
Received in revised form 28 December 2010
Available online 26 February 2011

Keywords:
Hybrid sol-gel films;
Rosemary extract;
Spin-coating;
Nanoclusters;
Fluorescence

ABSTRACT

Hybrid sol-gel films containing *Rosemary extract* nanoclusters embedded into hybrid silica network have been successfully synthesized using the sol-gel procedure by exploiting the template route, in association with an adequate spin-coating method. Formation of film precursor sols and effect of selected amounts of octyl trimethoxysilane and ethyl oleate succinic anhydride into the starting acid sols on the sol-gel product size have been evaluated by dynamic light scattering technique. The spectral characteristics of hybrid organic–inorganic films have shown that the multiple functional groups from *Rosemary extract* associated with residual Si–OH groups can cause the increase in the degree of physical interaction. The effect of hybrid sols meaning the silica precursors molar ratio and template concentration on the fluorescence of hybrid films has been also investigated. The fluorescence properties of synthesized films were found to be dependent on template and natural extract concentration. A higher amount of template resulted in doubling the fluorescence intensity in the 400–480 nm domain. The microstructural characteristics of the hybrid films revealed by atomic force microscopy have shown a homogeneous surface morphology with cluster-like structure. Hybrid silica films exhibit a periodic structure with cluster size less than 150 nm.

1. Introduction

The wide variability and versatility of the sol-gel processes have attracted particular attention of chemists and engineers due to the possibility to develop a large number of new materials (e.g. bulk materials and coating films) with valuable technical properties [1–3]. Among them, the investigation of hybrid films is a field of growing interest due to promising applications mainly based on submicronic organic and inorganic interpenetrating networks [4] that impart their functional properties to the final synthesized materials.

The synthesis and characterization of different kinds of films have been reported by several groups of authors. A recent study was devoted to the nanoporous SiO_2 film synthesis starting from an acid one-step and acid-base two steps catalyzed sols under the action of octyltrymethyl ammonium bromide template [5]. A similar research [6] has revealed that the siloxane thin film can be effectively prepared by using an acyl mono/di-saccharide through the same templated approach. Preparation and specific properties of hybrid poly(vinyl alcohol)/SiO_2 and phenylsilsesquioxane/TiO_2 coating films have been already reported [7,8]. Other authors have studied the development of ordered mesoporous silica thin films templated with a mixture of non-ionic and cationic surfactants [9] and alkyl glycosides [10].

All these derived silica films exhibit various properties such as high porosity [5], low dielectric properties [6,11], improved gas barrier [7], and optoelectronic properties [8] that can be readily tailored for development of new materials. As a result it became increasingly attractive to use the film in a variety of applications such as microelectronics [12], catalysis [13], biotechnology [14] etc. The possibility of introduction of optically active/photoactive molecules without their degradation, physically or covalently bounded in a hybrid sol-gel network has been increased over the last few years [15–17], since they excite much interest in the fluorescent sensor fields and for new material preparation. In addition to the large applicability, the homogeneous structure, high transparency and other specific properties of silica films are greatly dependent on the experimental conditions in a sol-gel process [18].

The preparation of thin films that contain organic active centers requires the optimization of some important parameters that govern the internal mesophase formation. For instance, during the film deposition onto a silicon/quartz substrate there are several processes [10] which occur in a short period of time with influence on the film quality:

- solvent evaporation under vacuum and operational parameters of spin coating process;
- organization and possible aggregation of template in the presence of siliceous species;
- rate of condensation of silica host that capture the organic species.

According to author's knowledge encapsulation of plant polyphenol mixtures and factors influencing the fluorescence properties in a homogeneous film have not been investigated yet. There is only one

* Corresponding author. Tel./fax: +40 213154193.
E-mail address: a.meghea@gmail.com (A. Meghea).

0022-3093/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.jnoncrysol.2011.01.018

study which discusses the incorporation of a polyphenol (epigallocatechin gallate) from green tea extract in layer-by-layer assembled films for construction of antioxidant assemblies as a protective element against free radical species [19].

Therefore, this study was devoted to the sol-gel synthesis of organic–inorganic hybrid films containing a vegetal extract (Rosemary Extract — RE) embedded inside silica host network and investigation of the fluorescence of the materials prepared from three types of sols, in which an octyltrimethoxysilane (OMEOS) and tetraethoxysilane (TEOS) were used as organic and inorganic silica precursors, while RE acts as organic fluorescent component. The two silica precursors, in different combinations, are used in the synthesis scheme of hybrid films by exploiting a templating route of sol-gel method which ensures an easy immobilization of RE, while preserving at the same time its active centers. As a template agent, an alkenyl succinic anhydride derivative (ASA, where alkenyl is the ethyl oleate, Fig. 1a), originated from natural vegetable oils (sunflower oil and rape oil) was used. Having in view the applications of ASA in several fields, including as hydrophobic and collagen agent or producing a thermoplastic protein film [20], it is interesting to study the behavior of this compound as template in sol-gel synthesis of hybrid silica films. We chose RE as active organic compound due to its well known health benefits [21,22], multiple active centers (OH, COOH, C = O) and since its components (Fig. 1b) are highly soluble in hydro-alcoholic solution that creates optimum conditions for its silica encapsulation.

2. Experimental details

2.1. Materials

Tetraethyl orthosilicate (TEOS, Aldrich, 98%) and Octyl trimethoxysilane (OMEOS, Aldrich, 96%) have been used as silica source, Ethyl oleate succinic anhydride (ASA derivate) as template agent, ethanol (Riedel-de Haën, 99.8%), and nitric acid (65%, Merck) as catalysts. The ASA derivate was offered by INP Toulouse, Laboratoire de Chimie Agro-Industrielle (France). Rosemary Extract (RE), a white greenish-yellow amorphous powder, was extracted from *Rosmarinus officinalis* L. and chemically identified using UV, IR, NMR and MS [23]. The main constituents are derivatives of rutin acid, gallic acid, caffeic acid and Rosemary acid. RE was supplied by National Institute for Chemical-Pharmaceutical Research and Development (Romania).

2.2. Synthesis

The preparation method is based on the conventional sol-gel technique with the hydrolysis of silicon organic compounds [24,25]. Sol-gel derived silica hybrid films were synthesized using an acid catalyzed hydrolysis of TEOS and OMEOS, simultaneous with polycondensation processes, in the presence of a succinyl alkenyl template agent.

2.2.1. Typical sol synthesis and RE immobilization

The initial sols and RE immobilization were obtained in two steps. Firstly, prehydrolyzed TEOS/OMEOS sols were prepared by mixing TEOS, OMEOS, Et-OH, H_2O and ASA. The precursor solutions were adjusted at an acid pH (pH ~3) with nitric acid in order to obtain a faster hydrolysis process. The molar ratios were varied in order to attain the production of good quality films with appropriate fluorescence properties. So, the final molar ratio for the acid precursor solutions were: TEOS:OMEOS:Et-OH:H_2O:ASA = 1:0.11:4:2:0.01 (denoted S1), 1:0.11:4:2:0.02 (denoted S2) and 1:0.15:4:2:0.02 (denoted S3), respectively. In the second step, the precursor sol solutions have been aged together with a hydro-alcoholic solution of RE at room temperature, for 12 h to allow a reinforcement of the porous frame of the sol and assure an adequate immobilization of RE inside the hybrid silicon network. The appropriate hydro-alcoholic solution obtained by solving 0.05 g RE in 10 mL Et-OH:H_2O (7.5:2.5, v/v) was added to 12 g acid sol. The final solutions have been denoted as S1-RE, S2-RE and S3-RE 1. For comparison purpose, a precursor sol which contains a higher amount of RE (0.08 g) embedded in hybrid network has been prepared and denoted S3-RE 2. The sols thus obtained were ready for coating at this stage.

2.2.2. Hybrid film preparation

The coating solutions described above (derived from S1, S2 and S3) were used for film deposition on a cleaned silica glass substrate by using the spin-coating procedure. The silica substrates were firstly embedded in a NaCl solution (6 mol/L) and ultrasonically cleaned for 15 min to remove the residues of silica. Secondly, the substrates were ultrasonically cleaned (three times) in bidistilled water for 15 min. Finally, they were heated at 450 °C for 2 h and then preserved in a dry desiccator for the deposition usage.

The S1-RE, S2-RE, S3-RE 1 and S3-RE 2 were uniformly dropped onto the cleaned silica surfaces. The spin coated films were obtained by applying a program in two steps: 1500 rpm for ± 40 s, followed by a further coating at 2000 rpm for 60 s, using a Spin coating equipment (Laurell-WS Model-400B-6NPP/LITE). The gel films thus obtained were dried in air at moderate temperature (45 °C) during 2 h in order to preserve the RE integrity and kept one week at room temperature to stabilize the network structure before subsequent characterization.

2.3. Characterization technique

The evolution of size distribution of the initial hydrolyzed and condensed silicon species from the three kinds of precursor sols were estimated by dynamic light scattering (DLS) technique using a

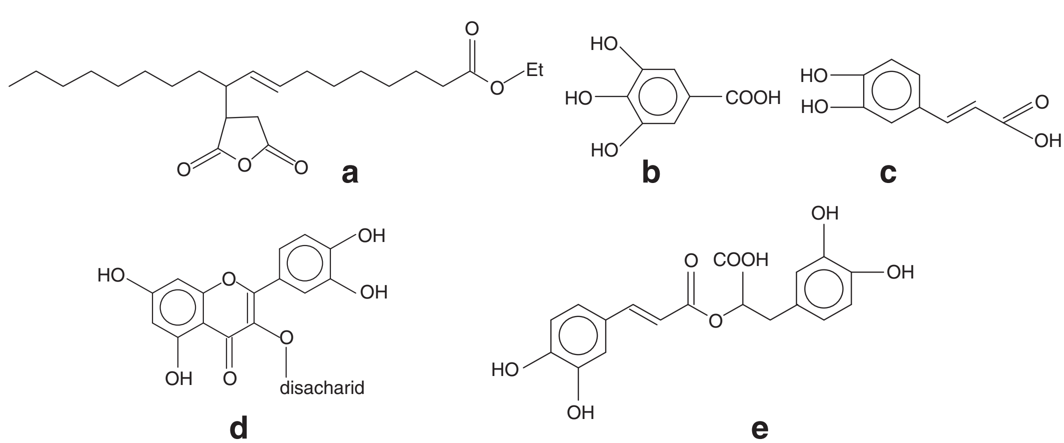

Fig. 1. Chemical structure of template agent and polyphenols from RE: Ethyl oleate succinic anhydride (ASA derivate) (a); gallic acid (b); caffeic acid (c); rutin (d); and Rosemary acid (e).