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Morphology and optical characteristics of hybrid matrix films with incorporated silver nanoparticles[♣]

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A simple procedure for the creation of thick hybrid films with metal nanoparticles is described. Ex-situ synthesized silver nanoparticles are incorporated in three hybrid matrix solutions, prepared by a sol-gel process. The hybrid matrix films, composed of PVA-PEG-B_2O_3, PVA-PEG-SiO_2 and PVA-PEG-SiO_2-B_2O_3, with and without incorporated silver nanoparticles, are obtained by a solution casting method at ambient temperature. The films with incorporated silver nanoparticles possess a yellow colour and a transparency suitable for optical applications. The structural interactions, surface morphology and optical properties of films are studied. The morphology of the films and the homogeneity of distribution and stability of the silver nanoparticles are strongly influenced by the components of the matrices. The silver nanoparticles aggregate completely in the pores of a porous polymer-borate hybrid film. The most homogeneous distribution of nanoparticles is observed in dense hybrid films containing silica.

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1. Introduction

In recent years, organic-inorganic hybrid materials, such as polymer-oxide films, have attracted considerable attention due to their improved physical, mechanical and thermal properties, compared with the pure polymeric material or inorganic oxide material. Sol-gel chemistry allows one to combine, at the nanosize level, inorganic and organic (or even bioactive components) in a hybrid composite. Hybrid materials containing nanoparticles are of interest for many research areas, because, in addition to the molecular inorganic-organic network (matrix), the material is also tailored by the physical, electronic, optical and catalytic properties of the nanoparticles [1, 2].

In this paper, we report the fabrication of sol-gel based hybrid matrix films composed of PVA-PEG-B_2O_3 (matrix M1), PVA-PEG-SiO_2 (matrix M2) and PVA-PEG-SiO_2-B_2O_3 (matrix M3), with and without incorporated silver nanoparticles (Ag-NPs). These hybrid films are obtained by a solution casting method, and characterized by Fourier Transform Infrared spectroscopy (FT-IR), Scanning Electron Microscopy (SEM), and Ultraviolet-visible absorption spectroscopy (UV-vis).

2. Experiment

Fig. 1 summarizes the overall synthetic procedure developed to obtain homogeneous hybrid matrix films, with and without incorporated Ag-NPs.

Analytical grade silver nitrate ($AgNO_3$), boron acid (H_3BO_3), ethanol 96% (EtOH) and hydrochloride acid 37 % (HCl) were purchased from the Laboratory of High Purity Substances, University of Sofia. Tetraethoxysilane 99% (TEOS) was purchased from Fluka, Germany, while polyvinyl alcohol 72000 (PVA) and polyethylene glycol 400 (PEG) were from Sigma-Aldrich Chemie, Germany.

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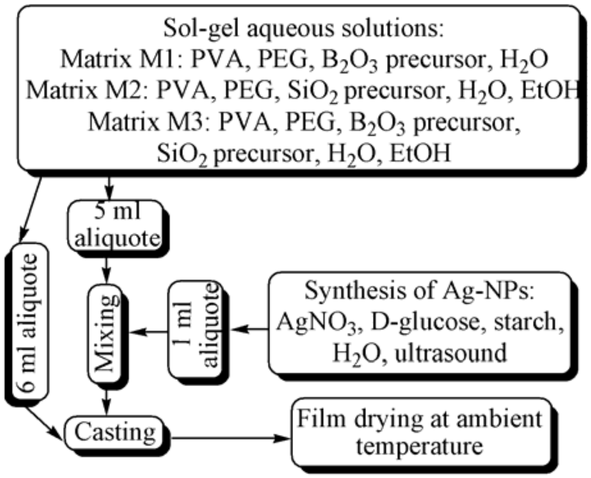

Fig. 1. Scheme of the overall synthetic procedure adopted to obtain hybrid matrix films, with and without incorporated Ag-NPs.

The hybrid matrix solutions were prepared by a sol-gel method [3]. Stock solutions of 4 wt. % PVA_{72000}, 4 wt. % H_3BO_3, and pre-hydrolysed TEOS (in a water-alcohol medium acidified by 5 % HCl (pH 3-4)) were prepared in double distilled water from commercial chemicals. Transparent gels of the following mass ratios were formed:

M1: PVA : PEG : B_2O_3 = 22 : 16 : 1;
M2: PVA : PEG : SiO_2 = 3.5 : 0.5 : 1;
M3: PVA : PEG : SiO_2 : B_2O_3 = 28 : 2 : 8 : 1

Silver nanoparticle dispersions (0.5 mM) were pre-synthesized by ultrasound-assisted reduction of $AgNO_3$ (20 µL 0.1 M), using soluble starch (4.2 mL 0.2 wt %) as a protecting agent and D-glucose (50 µL 0.1 M) as a reducing agent under basic conditions (100 µL 0.1 M NaOH). The dispersions were used without any further concentration or modification.

Ex-situ synthesized Ag-NPs were dispersed by sonication into the sol-gel hybrid matrix solutions at a volume ratio of 1:5, and stirred for about 30 min at room temperature. The aliquotes of the resulting homogeneous solutions, as well of the blank matrix solutions (without nanoparticles), were cast onto glass plates. The films were allowed to dry at ambient temperature for one week, and the dried films were subsequently peeled off. The thicknesses of the films depended on the matrix composition, and were in the range 24-48 µm (±5 µm), measured by a micrometer.

FT-IR was used to provide information on structural changes caused by the modification of polymer-borate matrix M1 with silica, and to assess the interaction between the silver NPs and hybrid matrices. FT-IR spectra of the hybrid films were obtained using a Bruker Tensor 27 instrument, in air. The blank hybrid films and films with incorporated Ag-NPs were studied for morphological variations, using a JEOL JSM 5510 scanning electron microscope. The UV-vis absorption spectra of the nanoparticle dispersions and hybrid films were measured with a Jenway (model 6400) spectrophotometer in the range 320 to 1100 nm, and with a Unicam UV 530 spectrophotometer in the range 200 to 900 nm. Individual silver nanoparticles were observed with a JEOL-1011 transmission electron microscope.

3. Results and discussion

The TEM image presented in Fig. 2 shows that the pre-synthesized Ag-NPs are nearly spherical, with a mean diameter of 39.5 nm (± 1.3 nm). The narrow absorption peak at 413 nm is the typical band associated with the surface plasmon resonance (SPR) of conduction electrons in small spherical silver clusters.

Fig. 3 shows FT-IR spectra of the blank hybrid films which are compared with the spectra of films with incorporated Ag-NPs. The characteristic bands of polymer components are observed in all FT-IR spectra: ν(C-H) at 3000-2800 cm^{-1}, δ(C-H) at 1470-1370 cm^{-1}, δ(O-H) and ν(C-O-C) at 1300 cm^{-1} and 1100-1000 cm^{-1} respectively, and ν(C-H_2) at 2940 cm^{-1} [4,5]. The very strong broad band in the region 3600-3200 cm^{-1} is ascribed to O-H bond stretching of the polymers.

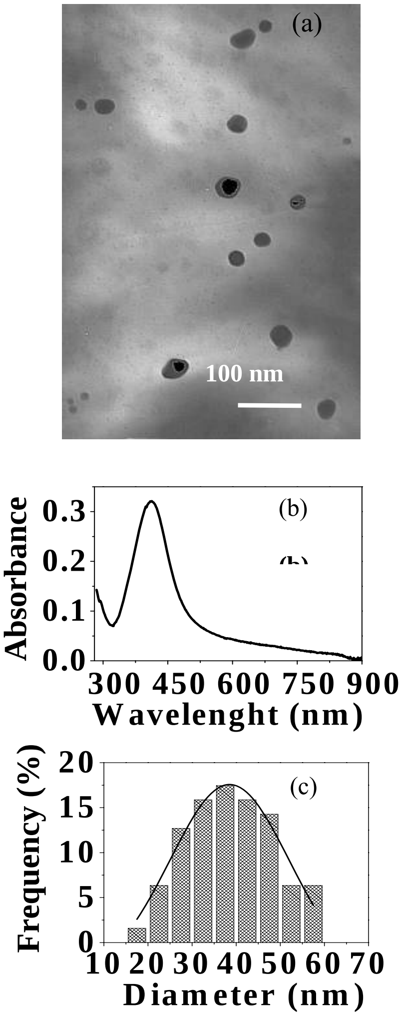

Fig. 2. (a) TEM image of Ag-NPs. (b) Optical absorption spectrum of the same NPs dispersion. (c) Particle size distribution evaluated using Image J software.

In the FT-IR spectra of the hybrid film M1, with and without nanoparticles, the bands at 1200-850 cm^{-1} and 1500-1200 cm^{-1} are assigned to the borate units BO_4 and BO_3, respectively. Only incomplete conclusions regarding the structure can be made, due to the very high intensity of the band at 1200-850 cm^{-1}. Compared to the FT-IR spectrum of the blank hybrid film M1, the profile of the multiplete band at 1300-1200 cm^{-1} is changed in the spectrum of the M1 film with incorporated Ag-NPs: the relative intensity of the bands decreases and the absorbance maxima split after such incorporation, thus suggesting partial transformation of BO_3 to BO_4 units [6].

Compared to the FT-IR spectra of both the blank hybrid films M1 and M2, the appearance of a new band at 665 cm^{-1} in the FT-IR spectrum of the blank hybrid film M3 is attributed to the formation of B-O-Si bridges [7]. This band is also observed in the FT-IR spectra of the hybrid film M3 with incorporated Ag-NPs. It is a possible reason for the surface morphology evolution of the films M3 within a month, as observed in Fig. 4c.

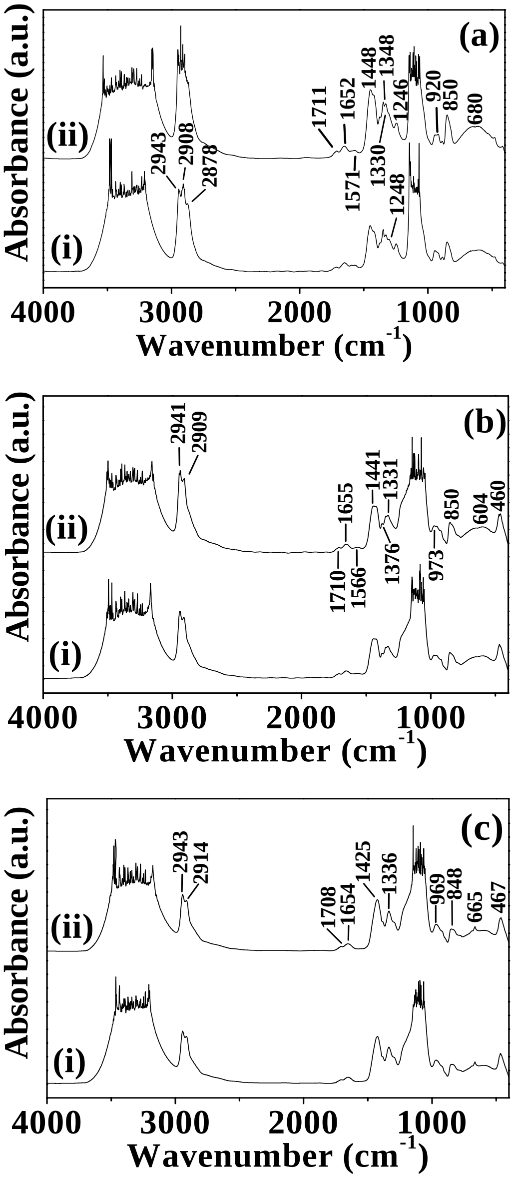

Fig. 3. FT-IR spectra of (a) M1, (b) M2, (c) M3 hybrid films: (i) with and (ii) without nanoparticles

The identity of the FT-IR spectra of the two blank hybrid films M2 and M3 with the spectra of these films with incorporated Ag-NPs proves that there are no significant structure changes in the hybrid matrices M2 and M3 due to the nanoparticles.

SEM images of hybrid films with and without silver nanoparticles, taken right after the preparation and after a month of storage, are shown in Fig. 4. The higher PEG content in the hybrid matrix M1 is the possible reason for the big pores (mean pore diameter 720 nm (± 25 nm)) and surface roughness of this film (Fig. 4a,i). The polyvalent alcohols PVA and PEG are 1,3 - and 1,n - diols respectively, and probably PEG is cross-linked with bigger pores than PVA. The presence of silica in the hybrid films

M2 and M3 prevents the formation of big pores, and leads to the formation of dense and homogeneous films with smooth surfaces (Fig. 4b,i and c,i).

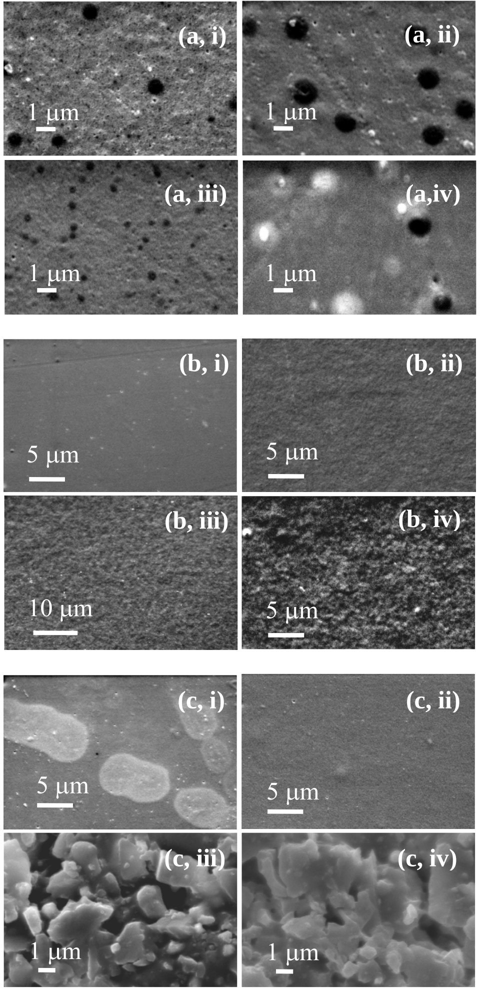

Fig. 4. SEM images of (a) M1, (b) M2, (c) M3 hybrid films: (i), (iii) – blank hybrid films; (ii), (iv) - films with incorporated Ag-NPs. Micrographs (i) and (ii) were taken right after the film fabrication; (iii) and (iv) - after a month of film storage.

The UV-vis spectra of the hybrid films, recorded right after the preparation and after a month of storage, are shown in Fig. 5. As shown in the insets, a slight red-shift is observed after the incorporation of Ag-NPs in all sol-gel hybrid matrices, because of their higher refractive index [8]. A strong broadening of the absorption band, due to significant particle aggregation right after the film preparation, is observed only for the polymer-borate matrix M1. The UV-vis spectrum of the hybrid M1 film, recorded a month after its fabrication, shows no surface plasmon band associated with Ag-NPs. Indeed, the nanoparticles aggregate completely in the enlargement pores of the porous hybrid film M1 with incorporated nanoparticles (mean pore diameter 932 nm (± 10 nm)) within a month (Fig. 4a, iv).

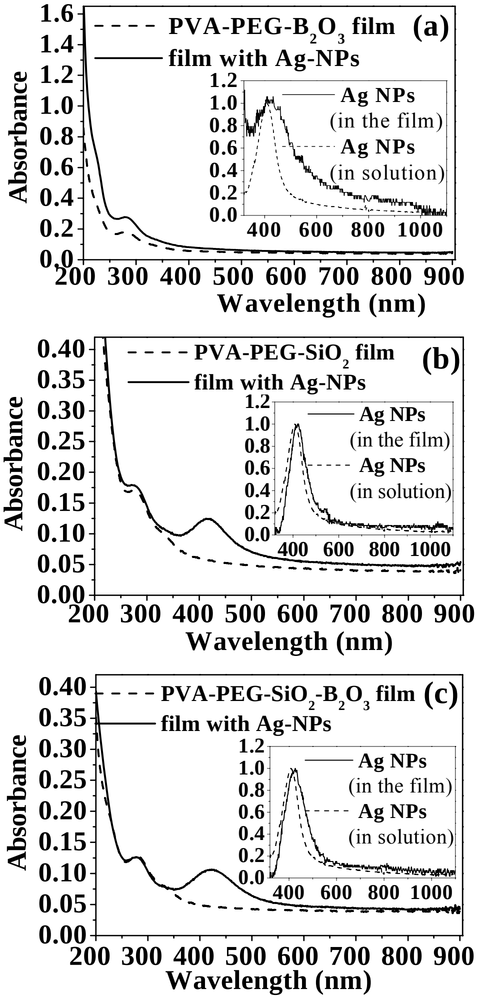

Fig. 5. Optical absorption spectra of (a) M1, (b) M2, (c) M3 hybrid films recorded a month after the fabrication. The insets show the absorption bands of Ag-NPs in the ex-situ synthesized dispersion and in the films recorded right after the fabrication.

The UV–vis spectra of hybrid films M2 and M3, recorded a month after their preparation, have shown a distinct characteristic absorption band. It is very clear that the silver nanoparticles incorporated in the dense hybrid M2 and M3 films are highly stable and well dispersed. Silica added into the hybrid matrix M3 seems to prevent the pore formation and hence the aggregation of Ag-NPs. This is in accord with the SEM images of the respective films in Figs. 4b and c.

4. Conclusions

Pre-synthesized silver nanoparticles were incorporated in hybrid films containing polymers (PVA and PEG) and boron oxide, silicon oxide or both oxides simultaneously.

This gave fully transparent films with a yellow coloration. The surface morphology, homogeneity of spatial distribution and stability of silver nanoparticles in the hybrid films were strongly influenced by the components of the matrices. The silver nanoparticles aggregated completely in the pores of the porous polymer-borate film. The most homogeneous distribution and high stability of nanoparticles was observed in the dense hybrid films containing silica.

There is a complex interplay between matrix composition, structure interactions, film surface morphology and optical properties that requires additional investigations of these films.

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