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Optical behaviour of sol–gel derived photonic structures formed by submicron silica spheres[*]

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Sol–gel synthesis of powders consisting of regularly shapedsubmicron silica spheres (∅400–600 nm) is described. IR and absorption spectra of such powders have been obtained. The IR spectra demonstrate that the silica spheres heated at 800 °C are hydroxyl-free. The TEM measurements show that the dimensions of silica nanoparticles do not change during heating. Films of self-organized silica nanospheres deposited on a glass support exhibit the photonic crystal effect.

Key words: silica submicron spheres, photonic effect, sol–gel method

1. Introduction

In the last decade synthesis and optical properties of photonic crystalline structures have been intensely investigated. Photonic crystals are characterized by frequency-forbidden band-gaps in a broad frequency region [1–4] of electromagnetic radiation. The characteristic feature of such materials is their opalescence. It has been demonstrated [5–9] that photonic crystals offer a number of potential applications such as filters, inhibitors of spontaneous emission or thresholdless lasers. Three-dimensional photonic crystals are typically formed by spatially arranged structures of closely packed submicron spheres. The most popular photonic structure is represented by opal formed by silica microspheres. Other examples of such photonic materials are microstructures built from polystyrene or latex microspheres. In this work, we report a sol–gel synthetic yielding regularly shaped silica microspheres which suspensions are capable of forming thin films exhibiting the photonic crystal effect. Preliminary spectroscopic investigations of the material obtained have also been performed.

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2. Experimental

The uniform silica particles were synthesized following the base-catalyzed polycondensation of silicic acid groups using tetraethoxysilane in alcoholic medium [10]. This procedure leads to formation of giant silica macromolecules. A mixture of 42 cm^3 of ethanol (99.6%) and 7.5 cm^3 of aqueous ammonia solution (NH_3, 25%, POCh, Gliwice) was mixed with 3.1 cm^3 of tetraethoxysilane (TEOS, 99%, Fluka). The solution was stirred in a plastic flask with a magnetic stirrer at room temperature for 1.5–2 h. We have also varied the synthetic conditions by adding different volumes of aqueous ammonium: 1.9 cm^3 (a), 3.75 cm^3 (b), 7.5 cm^3 (c), 11.2 cm^3 (d), 15 cm^3 (e). Then the material was left for solvent to evaporate. Powders were dried at 80 °C for three days. Such materials were then sintered at higher temperatures (200 °C for 16 h, 600 °C for 16 h and 800 °C for 16 h).

Photonic crystal structures were obtained by redispersing silica spheres in dimethyloformamide (DMF) and leaving them to naturally sediment on glass plates. The structures obtained exhibit opalescence characteristic to photonic crystals.

The silica spheres prepared were characterized by transmission (TEM) and scanning (SEM) electron microscopies. TEM studies were carried out on a Philips CM20 microscope operating at 200 kV and providing a 0.24 nm point-to-point resolution. SEM measurements were performed on a scanning electron microscope Joel JSM 5800LV. The absorption spectra were measured on a Ocean Optics 2000 spectrophotometer. The IR measurements were carried out at room temperature. Spectra were obtained with a Bruker IFS-88 FT spectrometer in the region of 4000–400 cm^{-1} with the resolution of 2 cm^{-1}. Polycrystalline powders were obtained by grinding in an agate mortar. Their suspensions in Nujol were placed between KBr wafers and the IR spectra were measured.

3. Results and discussion

TEM pictures of the products obtained with different amounts of aqueous ammonia (the catalyst) are shown in Fig. 1. The first picture (Fig. 1a) shows formless sol–gel silica glassy material obtained with 1.9 cm^3 of aqueous ammonia. Fig. 1b demonstrates silica powder consisting mostly of formless material with some single spherical particles. This sample was obtained with 3.75 cm^3 of aqueous ammonia. Further increase of the amount of aqueous ammonia results in the internal structure of the obtained powders becoming more regular and the particles gaining spherical shape. Fig. 1c shows the regular silica spheres (diameter ca. 415 nm) prepared using 11.2 cm^3 of aqueous ammonia. Similar materials have been obtained with 7.5 cm^3 (the spheres of diameter ≈ 600 nm) and 15 cm^3 (the spheres diameter ≈ 500 nm) of aqueous ammonia. It has been observed that the shape and size of the silica nanoparticles did not change with temperature. The TEM micrographs of the sample obtained with

11.2 cm^3 of ammonia solution (see Fig. 1c) heated at 200 °C, 600 °C and 800 °C are virtually identical.

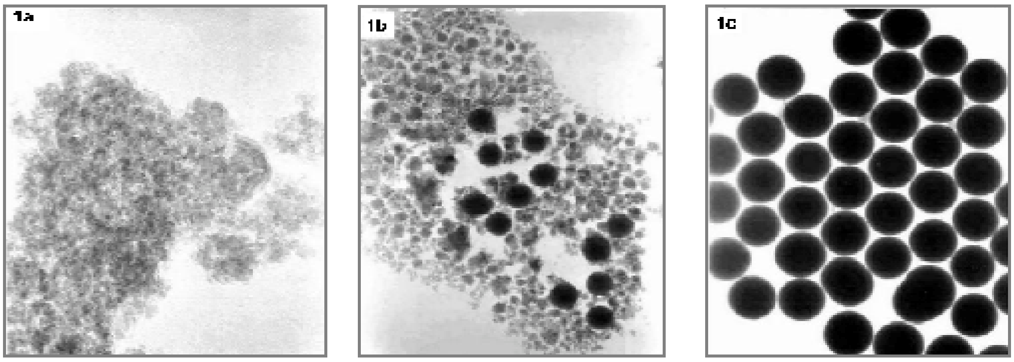

Fig. 1. TEM micrographs of the sol–gel powders obtained with different amounts of aqueous ammonia: a) 1.9 cm^3, b) 3.75 cm^3, d) 11.2 cm^3

Figure 2 presents the IR spectra of the silica spheres measured at the successive stages of the thermal treatment. As it can be seen, increase in temperature results in intensity decrease of the band at approximately 3400 cm^{-1} which indicates the diminishing in the hydroxyl groups content in the silica powder.

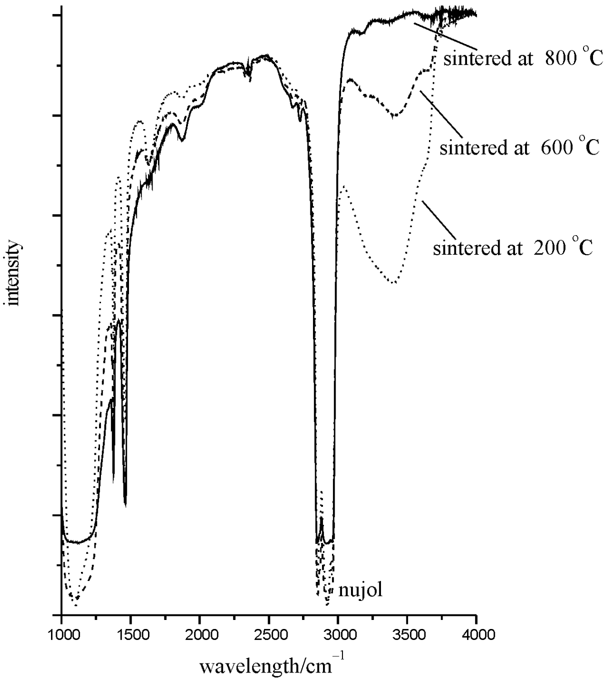

Fig. 2. IR spectra of the silica spheres sintered at different temperatures

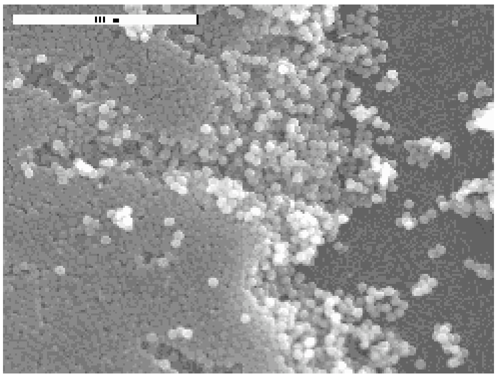

Fig. 3. SEM micrograph of a silica spheres on a glass support

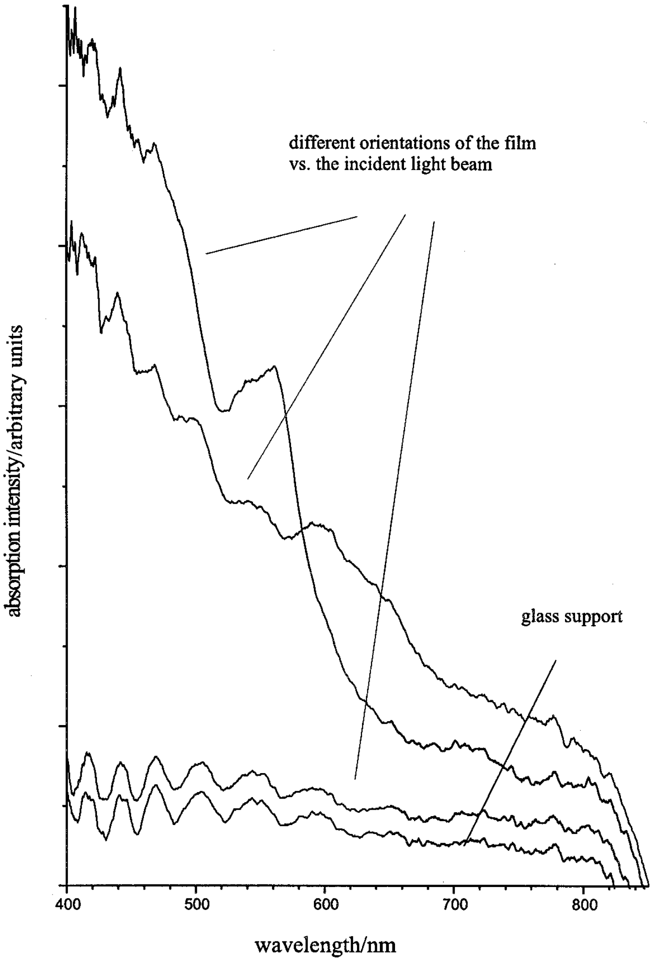

Fig. 4. Absorption spectra of a thin film of silica spheres on a glass support obtained at different angles between the film and the incident light beam

The silica nanospheres were placed on glass supports in the form of thin films. Figure 3 presents a SEM micrograph of such a film. The self-assembled films of silica spheres demonstrate strong opalescence. The absorption spectra of such films obtained at different orientations of the glass support versus the incident light wavelength are shown in Fig. 4. A shift of the absorption edge with the changes of the angle of the incident light can be seen. Since a thin film consisting of the uniform silica spheres has formed on the support in a random manner, changes of the film position in the light path result in random changes of the absorption edge (the sample's apparent colour). The same effect is responsible for random opalescence of natural opals. This effect demonstrates the photonic crystal character of the investigated materials.

4. Conclusions

The sol–gel-based method of preparation of submicron spherical silica particles is reported. The nanospheres morphology has been studied by the TEM method. It has been found that all silica particles possess uniform spherical shape and virtually identical size (ca. 400 nm). It has been observed that with increasing temperature of sintering water contamination was significantly reduced while the particles size remained unchanged. Photonic crystal behaviour of the films formed by silica spheres placed on planar glass supports has been observed.

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