Sol–gel derived metal oxides doped with silver nanoparticles as tunable plasmonic materials

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New composite materials made of transition metal oxides doped with silver nanoparticles are proposed. Titanium and zirconium dioxide matrices were prepared by sol–gel method adjusted for addition of silver nanodopants. Commercially available silver nanoparticles in the form of powder (30–50 nm) or colloidal solution (5–15 nm) were used for doping of oxide hosts. To recover plasmonic properties of silver after annealing in air, reduction of samples in the H2:Ar atmosphere was performed. As a result, the silver-containing TiO2 and ZrO2 films of good optical quality with plasmonic absorption near 400 nm were obtained. The potential of embedding of luminescent markers (like rare earth ions) into considered films is discussed.

1 Introduction The development of functional composite materials containing noble metal nanoparticles is leapfrogging now. It is due to the plasmonic activity of the metal nanoparticles which can drastically change the properties of the host media. Plasmonic effects initially discovered for the nanorelief surfaces of noble metals [1–3] become apparent also in the composite bulk materials in the vicinity of noble metal nanoparticles [4–6]. Electric field of the exciting light is enhanced nearby the metal nanoparticles at the plasmonic resonance wavelength. Such a local field with enhanced amplitude may be used for the resonance amplification of light absorption or scattering [7, 8], Raman scattering [9], and improving of nonlinear optical properties in the host matrices [4]. There are known cases of quenching [10–12] and amplification of fluorescence [7, 8, 13] under the action of plasmonic effects.

Control of plasmonic resonance wavelength and degree of its influence on the light absorption, scattering and fluorescence is essential for the optical science and applications. Using of noble nanoparticles with different sizes and shapes allows creating of composite systems with different spectral position of the plasmonic resonance wavelength [14]. But it is generally complicated to prepare nanoparticles with well-controlled size and shape. Another way lies in changing of the host matrix. Plasmonic resonance appears for the wavelength at which the module of permittivity for nanoparticle material is approximately twice higher then real permittivity of environmental host medium [4]. Thus changing of permittivity of the host medium allows tuning the wavelength satisfying the resonance condition.

Oxides of transition metals like TiO2 and ZrO2 are suitable as host matrices for the nanocomposites because of several reasons. On the one hand permittivities of TiO2 and ZrO2 hosts allow tuning of plasmonic resonance for noble nanoparticles in the region of visible light wavelengths. Thus TiO2 doped with gold and silver nanoparticles was considered earlier as nonlinear optical medium working in the visible light region [4]. On the other hand TiO2 and ZrO2 matrices doped with noble nanoparticles may be used as active media for incorporation of luminescent markers (like rare earth ions). Previous investigations revealed an effective fluorescence of Sm3+ ions in the TiO2 and ZrO2 hosts [15, 16]. Possibility of control rare earth fluorescence in TiO2 and ZrO2 matrices using plasmonic effects in noble nanoparticles looks attractively.

The aim of this paper is proposing of new plasmonic composite materials consisting of ZrO2 and TiO2 hosts doped with silver nanoparticles. Adaptation of sol–gel method to preparation of such systems is considered. Plasmonic absorption of obtained films is investigated. Potential applications of obtained films for the enhancement of fluorescence are discussed.
2 Materials and methods A sol–gel route based on hydrolysis and polycondensation of Ti(OBu)$_4$ (Alfa Aesar, 98 wt.%.) and Zr(OBu)$_4$ (Alfa Aesar, 80 wt.% solution 1-butanol) was employed for preparation of silver-doped TiO$_2$ and ZrO$_2$ media. Proper metal-oxide sol precursors were obtained by mixing solution containing distilled water and $n$-butanol (YA-KEMIA OY) with Ti(OBu)$_4$ (mole ratio 1:24:1.6) or Zr(OBu)$_4$ (mole ratio 1:24:1.6) and stirring the mixture for 1 h at 21°C [17].

Silver nanoparticles are expected to have plasmonic resonance in the visible violet region which would overlap with the absorption or emission transitions of many rare earth ions. Thus we selected silver nanoparticles (size 5–15 nm) dispersed in hexane (Aldrich) and silver nanopowder (size 30–50 nm) (Nanoamor). These nanoparticles were immersed into the previously prepared metal alkoxide precursors and ultrasonically treated by means of mixer UP 200S (Hielscher). Different concentrations of silver in the hydrolyzed metal alkoxide solutions were made in order to obtain finally oxides with 1, 4, and 8 wt.% of silver nanoparticles. Mixtures of metal alkoxide solutions with silver nanoparticles were spincoated on the glass plates at 4000 rpm during 2 min and gelled.

Structure of samples was studied by means of an optical microscope. Transmittance of obtained films was measured by using Jasco V-570 spectrophotometer. In some cases we applied to the films specific postproduction annealing procedures, which will be described in the next section.

3 Results and discussion It is well known that humidity and chemical composition of precursors may strongly influence on the structure and character of cracking in sol–gel derived materials [18]. Initial metal alkoxide solutions give possibilities for the formation both dense films by means of spincoating and non-spincoated xerogels. We found that the presence of silver nanoparticles inside the xerogel samples changed their cracking structure essentially.

Let us compare the microstructure of xerogels made of droplets of metal alkoxide solutions without (Fig. 1a) and with (Fig. 1b) silver nanoparticles. In the both cases in the xerogel structure one can see the fragments of radial cracks directed from the edge of the droplet to its center (center is marked by red circle). As the wetness is non-uniformly distributed from the edges to the center of droplet this may also cause non-uniform hydrolysis and condensation reactions. As a consequence there is a shrinkage of the material, a tensile stress, and a radial cracking of the film.

The radial cracks divide the sample without silver particles into radially oriented elongated bands (Fig. 1a). Although the bands in xerogel sample with silver nanoparticles are also radially distributed, they are shorter in length, and have a rectangular shape (insert in Fig. 1b). There are several possible reasons for such rectangular structure. The presence of silver nanoparticles causes additional defects in the structure of initial droplet which may provoke cracking in concentrical direction. Authors of Ref. [19] report about similar rectangular cracks observed in the structure of platinum films deposited on different polymer surfaces. Such cracking is attributed to tension forces on the surface in the direction perpendicular to the radial cracks and surface buckling instabilities. Silver nanoparticles and their self-organizing may cause such additional surface tension forces and buckling in the sol–gel medium. Self-organizing processes in sol–gels doped with nanoparticles may be an object of separate future investigation which is beyond the scope of this paper.

Thin films without strong cracking were obtained after spincoating of metal alkoxide solutions on the glass slabs. Dependence of the transmittance $T$ of films vs. the...
wavelength of exciting light \( \lambda \) has interference character (Fig. 2). The fitting of the experimental dependences \( T(\lambda) \) using the methods proposed in Refs. [20, 21] allowed to estimate refractive indices and thicknesses of obtained films. Refractive indices of the films were in the range 1.8–1.9 and their thicknesses were \( \approx 200 \) nm. Interference patterns for films made of neat metal alkoxide solutions and solutions containing silver nanoparticles (8 wt.%) differ from each other in the short-wave range (Fig. 2, curve 1 and curve 2). The sample containing silver nanoparticles has a strong absorption band around 438 nm which is close to the wavelength of plasmonic resonance for silver [2].

In order to employ the plasmonic absorption to the enhancement of fluorescence (e.g., rare earth dopants) the release of organic traces and the formation of transparent crystalline medium is necessary. Presently, annealing of films in air at 500 °C during 1 h was applied. Such annealing promotes formation of clear TiO\(_2\) and ZrO\(_2\) medium and burning the rest of butanol from the films. Porosity and thickness of the films are slightly changed during this annealing. As a result, the wavelength of the plasmonic resonance is expected to shift from the initial position corresponded to non-annealed film.

Surprisingly after annealing the plasmonic absorption in the film with silver nanoparticles was disappeared (Fig. 3). Annealing in air may oxidize the surface of silver nanoparticles and eliminate its plasmonic activity. Thus a procedure of recovering of silver nanoparticles is necessary. Several manners of similar recovering are described in Refs. [4–6]. On the one hand recovering procedure must renew the silver nanoparticles. On the other hand this procedure must avoid formation of excessive amount of oxygen vacancies or reduced oxides, like Ti\(_2\)O\(_3\), which has non-transparent dark-violet color. After several attempts we found the appropriate recovering procedure. Films were cured in H\(_2\):Ar (1:3) atmosphere at 500 °C during 1 h and then cooled during 10 h. Plasmonic absorption in films TiO\(_2\) and ZrO\(_2\) doped with silver was recovered after such recovering procedure (Fig. 4). The maxima of plasmonic absorption bands for recovered TiO\(_2\) and ZrO\(_2\) based films have shifted to 403 and 405 nm, respectively.

Applications of sol–gel materials doped with nanoparticles of noble metals are developed now. Optical applications are mainly connected with the sol–gel derived coatings and waveguides working in the infra-red region [5, 6]. For example, silver nanoparticles have been incorporated into SiO\(_2\):Er in order to amplify some absorption lines of Er\(^{3+}\) and therefore enhance the fluorescence of the rare earth ion [6].

It would be an attractive idea to enhance fluorescence in the visible region by similar way. The observed plasmonic resonance of silver in TiO\(_2\) and ZrO\(_2\) overlaps with the most intense absorption bands of rare earth ions Eu\(^{3+}\) (\( ^7F_0 \rightarrow ^2G_{5/2} + ^3L_{6} \), \( ^7F_1 \rightarrow ^5L_{6} + ^5D_{2} \)) and Sm\(^{3+}\) (\( ^6H_{5/2} \rightarrow ^4F_{7/2} + ^4P_{5/2} + ^4K_{1/2} + ^4L_{1/2} \)) [22]. The rare earth ions are known to fluoresce efficiently in TiO\(_2\) and ZrO\(_2\) matrices in the visible region [15, 16]. As it was shown in Refs. [10–12] it is possible to achieve both the enhancement as well as the quenching of the fluorescence in the vicinity of noble metal.
nanoparticles. Generally speaking, influence of noble metal nanoparticle on the fluorescence is determined by the distance between nanoparticle and the emitting molecule. At close distances (a few nanometers) the non-radiative energy transfer from fluorophore to nanoparticle prevails. Enhancement of fluorescence in the vicinity of noble metal nanoparticle is possible, when the fluorophore molecule is placed at the distances 5–20 nm from the nanoparticle [11, 12]. Therefore incorporation of fluorescent dopant into the host matrices must be quite accurate in order to achieve necessary arrangement. Investigation of the fluorescence enhancement of rare earth emission in the TiO$_2$ or ZrO$_2$ hosts containing silver nanoparticles is in progress.

4 Conclusions We developed the preparation method for TiO$_2$ and ZrO$_2$ based media doped with silver nanoparticles. Both xerogel and dense film coatings were obtained. TiO$_2$ and ZrO$_2$ xerogels doped with silver nanoparticles show special cracking structure connected with additional surface tension admittedly caused by nanoparticles. Dense thin (~200 nm) TiO$_2$ and ZrO$_2$ films without strong cracking were obtained by means of spincoating. In addition to the traditional sol–gel procedure and annealing in air it is necessary to anneal the films in H$_2$:Ar atmosphere in order to recover the plasmonic resonance of silver nanoparticles. The obtained films have pronounced plasmonic absorption bands with maxima near 400 nm which may be slightly adjusted by using of different annealing and recovering treatments. Such films might be useful as improved hosts for fluorescent dopants on the assumption of precise controlling of the distance between fluorophore molecules and silver nanoparticles.

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