Nano-structured Organically Modified Silica Thin Films for Functional Surfaces

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ABSTRACT

We report a template-free sol-gel method for preparation of nanoporous ormosil thin films at ambient conditions. The thin films are coated to the surfaces by using colloidal suspensions of ormosil gels. Gels are synthesized by using a trifunctional organosilane monomer, methyltrimethoxysilane (MTMS), with a two-step acid base reaction. We prepared several ormosil thin films on glass, metal, plastic and paper surfaces with different functionalities like superhydrophobic, antireflective, antifogging and ice retarding properties, from gels prepared in different conditions. Also films on flexible substrates exhibits durable surface properties after several bending cycles. In addition, we also demonstrate that these thin films can be used for fluorescent sensing of explosives by doping them with fluorescent dyes.

Keywords: ormosil, nanoporous, superhydrophobic, antireflective, fluorescent sensor

1 INTRODUCTION

Sol-gel process enables mixing organic and inorganic components in the same matrix at the nanometer scale due to the mild reaction conditions [1]. Organically modified silica (ormosil) nano-composites are unique examples of such hybrid materials which offer best of the both of organic polymers and inorganics, like mechanical flexibility together with good chemical durability [2]. Flexibility is provided by covalently bonded organic groups with decreasing cross linking of the rigid silica network. Also it is possible to tune the physical properties of these materials by changing the organic group and its concentration [3]. Nano-porosity adds this hybrid materials extra-functionality such as high surface area and adsorption capacity, very low refractive index and low dielectric constant. Furthermore, producing nanoporous ormosils as thin films enables exploiting the intrinsic properties of thin films such as better transparency, control of thickness and composition, and deposition as multilayer films [4].

Nanoporous ORMOSIL films are typically prepared by using a solution of a silsesquioxane polymer in an organic solvent with a sacrificial polymer or porogen, which act as the pore generator via phase separation at the nanometer scale [5]. To realize nanopores the film is calcinated at high temperatures (400-450 $^{\circ}$C) to decompose and volatilize the pore generator. In an alternative method, periodic mesoporous organosilica (PMO) thin films were produced by polymerizing organically modified silicon monomers in the presence of surfactant molecules in acidic alcohol solutions [6]. Surfactant molecules must be removed after thin film deposition by calcination or by using acidic solutions to generate pores. Although uniform films with good thickness and porosity control can be produced with these methods, harsh template molecule removal steps limit the choice of substrate as mostly silicon and glass. On the other hand, substrates like plastics and paper, which are frequently used in low cost and flexible electronic, optoelectronic and photovoltaic devices, can easily damage or decompose at these conditions. Thus, new methods are strongly desired to produce nanoporous ormosil thin films at mild conditions.

In this context, template-free methods are promising to produce nanoporous ormosil thin films at room-temperature and neutral pH conditions by eliminating the challenging template removal step. Template-free methods result in random, well-accessible, cylindrical, and branched pore structure, and their porosities are generally higher than the template synthesized counterparts (reaching 98%) [7]. In template-free methods first, a porous gel is synthesized by using generally alkoxysilane monomers. Then the gel solvent is evaporated carefully to preserve the gel network. If the gels are dried under atmospheric conditions most of the pores are collapsed due to the high capillary pressure formed during solvent evaporation [8]. To prevent pore collapse gels (or thin films) are dried in supercritical conditions, which complicates the overall procedures. Prekash et al. [9] successfully prepared highly porous silica thin films at ambient conditions, by modifying the surface of common silica gel network with hydrophobic groups, which prevent pore collapse during solvent evaporation. However, these template-free methods have been reported only for common silica thin films, which result in inflexible network.

In our works, we used ormosil gels to produce flexible and nanoporous thin films. Ormosil gels are synthesized by polymerizing previously hydrolyzed methyltrimethoxy-silane (MTMS) monomer in basic conditions in different solvents. The produced gels are intrinsically hydrophobic due to the non-hydrolysable methyl groups of MTMS monomer. Thus, gels, appropriate for nanoporous thin film deposition at ambient conditions, can be obtained in one step by eliminating the surface modification. Then, the gel network is broken down by sonication to produce colloidal suspensions which are suitable for thin film preparation with common thin film deposition methods like spin, dip or spray coating.

Our template-free preparation method of nano-porous ormosil thin films enables large-area preparation of these films on almost any substrate including heat sensitive plastic and paper substrates. The ormosil colloidal suspensions can be deposited as homogeneous thin films with good thickness (90-1000 nm) and porosity (30-86%) control. These suspensions offer easy handling and good reproducibility for large-area fabrication of homogenous nanoporous and flexible thin films. We recently reported preparation of highly transparent and flexible superhydrophobic [10] surfaces and dye doped highly porous ormosil thin films for TNT sensing application [11]. Also we prepared ultrathin and uniform nanoporous ormosil thin films by using newly synthesized homogenous ormosil gels [12, 13]. The films exhibit durable antireflective properties on flexible substrates. Furthermore, we observed that by adding small amounts of co-monomers it is possible to tune the surface roughness and prepare completely transparent superhydrophobic surfaces [14].

2 RESULTS AND DISCUSSION

MTMS is known to result in opaque gels when polymerized in alcohols. This stems from macroscopic phase separation of cyclic and cage like polymerization products of MTMS which causes scattering of light [3]. Thus, in order to obtain a transparent gel, one must prevent phase separation. We can obtain transparent MTMS based gels by using dimethylsulphoxide (DMSO) as solvent instead of alcohol or by addition of tetraethylorthosilicate (TEOS) as co-monomer when the solvent is alcohol. This indicates solubility of polymerization products of MTMS in DMSO which are insoluble in methanol causing phase separation. In the case of addition of co-monomer the resulting polymerization products also change. As the forming gels are transparent we can say that these polymerization products are soluble in methanol. Transmission Electron Microscope (TEM) images of films, which are obtained from MTMS gels formed in methanol, DMSO and in methanol using co-monomer, also confirm the presence of phase separation for the former case. According to TEM analysis, size of ormosil cluster domains are around 20-30 nm for the gel with MTMS in methanol and it is around 3-5 nm for the other two (data not shown). By using above methods, we prepared several phase separated and homogenous gels to produce coatings with different functionalities. For thin film deposition, we prepare colloidal suspensions by sonication of gels with addition of alcohol. Obtained suspensions can be directly applied to the surfaces without requiring any post treatments. Furthermore, obtained suspensions can be applied to almost any surface including glass, plastics, cotton and metal surfaces using common coating techniques such as spin, dip and spray coating.

The ormosil thin films obtained by using MTMS monomer on glass substrates by spin coating are characterized by using low vacuum mode of Environmental Scanning Electron Microscope (SEM). Films obtained by using gel prepared in methanol (Fig. 1a) and gel prepared in DMSO (Fig. 1b) are found to be morphologically very different. The film obtained from gel prepared in methanol results in formation of larger pores which are mainly micrometer scaled, where the film obtained from gel prepared in DMSO is mainly composed of nanometer scaled pores. Furthermore the surface coverage of the DMSO based thin film is more homogeneous. There are uncoated sites present in the methanol based thin film which shows correlation with non-homogeneous gel formation. The films obtained from co-monomer used gels also have homogeneous surface coverage and they are composed of nanopores like DMSO based films. The effect of non-homogeneity of films obtained from MTMS gels in methanol can also be seen from Atomic Force Microscopy (AFM) measurements. AFM results indicate that the surface roughness is in the order of 120 nm for the films obtained from MTMS gelled in methanol, while it is around 5 nm for the other two cases (data not shown).

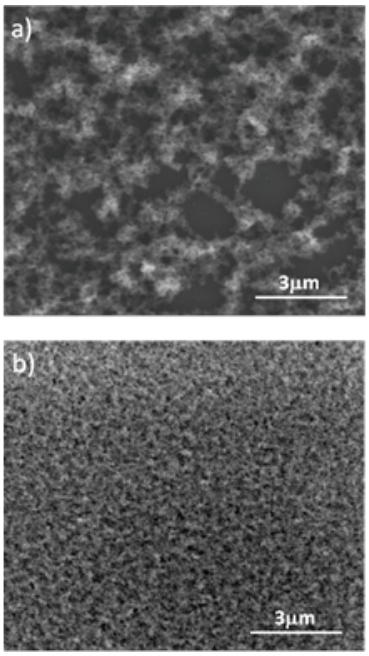

Figure 1: SEM images of ormosil thin films prepared by using gels synthesized in different solvents (a) methanol, (b) DMSO.

The thickness and the refractive index of the ormosil films are ellipsometrically measured. Figure 2 shows the dependence of refractive index with respect to MTMS concentration of the films obtained using DMSO as the solvent. As expected, the index of refraction decreases as the MTMS ratio decreases linearly. The index of refraction varies from 1.28 to 1.14 for DMSO/MTMS (v:v) ratios varying from 4 to 15. The same behavior is also observed for co-monomer containing thin films. Their refractive index is found to change linearly in the range of 1.23 to 1.17 by varying the TEOS:MTMS fraction. Tunable

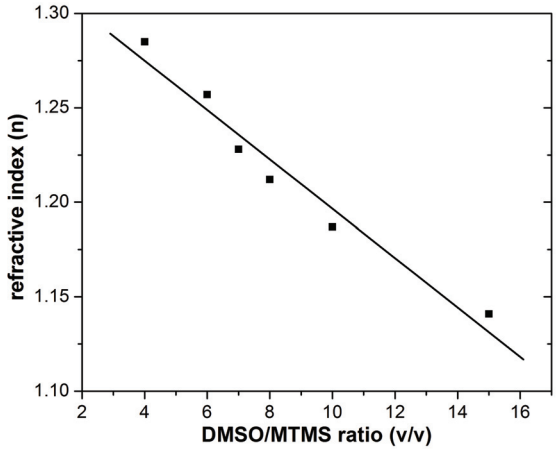

Figure 2: Refractive index change of the ormosil coatings with changing monomer concentration.

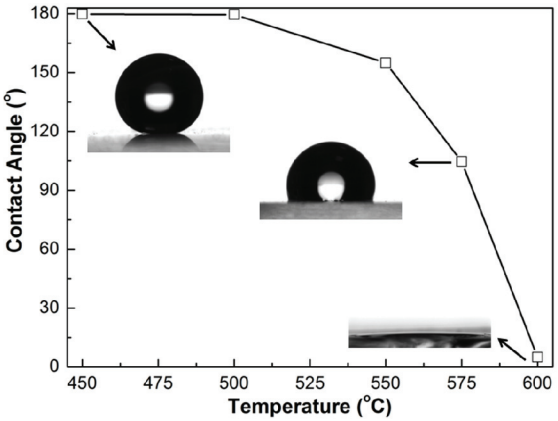

Figure 3: Water contact angles of annealed ormosil films at different temperatures.

refractive index of the films enables designing special coatings for substrates with specific refractive indices in order to enhance light transmittance.

Different from homogeneous gels, MTMS based gels prepared in methanol result in films with superhydrophobic character. Superhydrophobicity arises from high surface roughness of these films with combination of non-hydrolysable and hydrophobic methyl groups of the monomer. These films exhibit very high contact angles reaching 179.9° and they are found to be thermally very stable (Fig. 3). They are found to preserve their superhydrophobic character (155°) even after annealing at 550 °C for 1 hour. They are found to become superhydrophilic after annealing at 600 °C for 35 minutes. This is a result of replacement of hydrophobic methyl groups by hydrophilic hydroxyl groups. Besides their superhydrophobic property these films also exhibit anti-icing property. When super-cooled water is poured onto cooled plain glass and superhydrophobic ormosil coated glass, ice formation takes place on uncoated glass from everywhere while it takes place in the coated substrate only from the uncoated side walls.

The high porosity of the ormosil thin films allows molecules to easily access the inner parts of the material resulting in very high diffusion rates. Such high-porosity hybrid support structures would be essential in sensing and catalysis applications. In previous work, we report that, fluorescent dye doped nanoporous ormosil thin films can be used for rapid detection of gaseous phase trinitrotoluene (TNT), which is a common explosive. The gel is prepared by polymerizing MTMS in methanol and a porphyrin derivative is used as fluorescent dye. Fluorescent molecules are physically encapsulated in the ormosil network during gelation. The absorption and fluorescence spectra of fluorescent molecules in ethanol and the ormosil thin films were identical which proves the successful doping of ormosil thin films with fluorescent dye without significant agglomeration of dye molecules. Furthermore, fluorescence intensity of the films was found to be same even after 3 months, proving the successful fixing of the dye into the ormosil network. The fluorescence intensity of the films quench when they are exposed to the TNT vapor because of the photo induced electron transfer between TNT and porphyrin molecules. In Fig. 4, fluorescence quenching response of porphyrin doped ormosil thin film with an average thickness of 120 nm is shown. The film was found to have quenching efficiencies of 8.6% in 10 s and 28.2% in 60 s. SEM analysis shows that film includes both nanometer and micrometer sized pores (data not shown). This bimodal pore structure results in a high quenching efficiency. For control experiments a nonporous thin film was also produced and very low quenching efficiency (<1%) was observed as expected. Also we observed that quenching efficiency is highly thickness dependent. Lower quenching efficiencies observed for thicker films because of the decreasing micrometer sized pores.

Anti-reflective coatings are designed to decrease the back reflection from optical surfaces, which is undesirable because it usually decreases the device performance. To prepare an anti-reflective coating two conditions must be satisfied; i) refractive index (n) of the film must be selected as $n_c = (n_0 n_s)^{1/2}$ (where; n_c, n_0 and n_s are refractive indices of coating, air and substrate respectively) and ii) the thickness

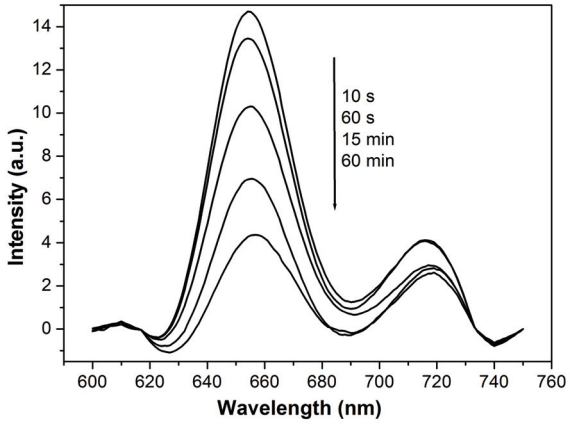

Figure 4: Fluorescence quenching response of dye doped porous ormosil thin film against TNT exposure.

of the film must be a quarter of the effective wavelength of light. For glass substrates (n = 1.5) at visible wavelengths,

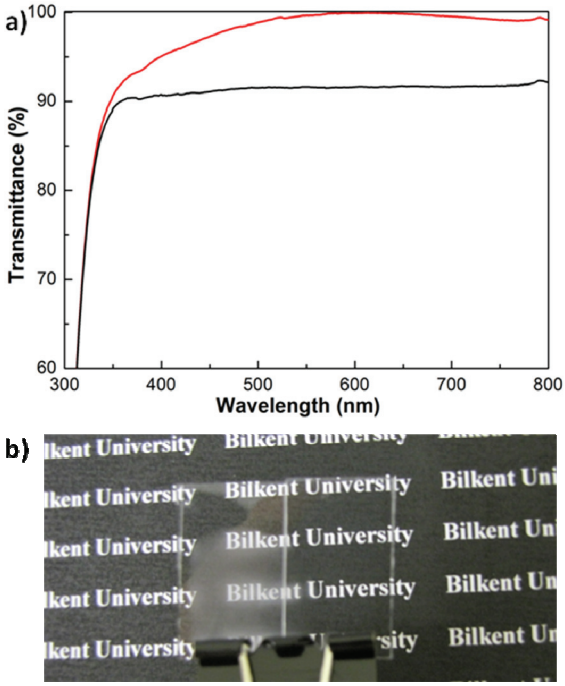

Figure 5: (a) Transmission spectra of glass substrate (black and ormosil coated glass substrate (red) (b) Photograph showing the antifogging property of annealed ormosil coating on glass.

refractive index and thickness of the film must be selected as around, 1.23 and 100 nm, respectively. The ormosil thin films produced by using gels synthesized in DMSO and with TEOS co-monomer are suitable for production of antireflective coatings because of their low surface roughness, uniformity at low thicknesses and tunable porosity. In Fig. 5a transmission spectra of glass substrate and ormosil coated glass substrate is shown. Transmission of ormosil coated glass slide reaches 100% at 600 nm where transmission of uncoated glass is only 91.3%. We also prepared antireflective coating at flexible substrates and we showed that durable antireflective property after 100 cycles of bending, with a bending radius of ~1 mm. In addition, films can be transformed to superhydrophilic by annealing at 600 °C and exhibits antifogging behavior without any loss in antireflective property (Fig. 5b).

3 CONCLUSIONS AND OUTLOOK

In summary, we established a facile template-free method for large area fabrication of ormosil thin films on any substrate with different functionalities. We prepared superhydrophobic surfaces by adjusting the surface roughness of the films and very high water contact angles (up to 179.9°) and very low sliding angles (<1°) are obtained. Also, the films on flexible substrates exhibited superhydrophobic behavior after bending multiple times indicating durable self-cleaning property. Furthermore, films exhibit anti-icing properties. When super-cooled water is poured on cold film coated glass slides water droplets slide from the surface while ice formation is observed for the bare glass slides. We also prepared antireflective coatings by preventing the macroporosity of the films via using different solvents or co-monomers. The films can be prepared as thin as 90 nm with pores smaller than 50 nm and refractive indices around 1.23 enabling preparation of antireflective coatings. We characterized the antireflective properties of the films on glass and plastic substrates and demonstrate mechanically durable antireflective performance under excessive bending. In addition, we also demonstrate that these thin films can be used as supports for sensors. We doped these films with a TNT sensing dye and observed fluorescence quenching based sensing of TNT. Furthermore, very recently we prepared completely transparent superhydrophobic surfaces by adding small amounts of co-monomers during gel synthesis.

We believe our room-temperature synthesis of nanoporous ormosil thin films will be essential in many applications, e.g. in low cost optical and electronic devices, solar cells, chemical and biological sensors, lab on paper devices where anti-reflective, hydrophobic, low dielectric constant and nano-porosity properties are critical.

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