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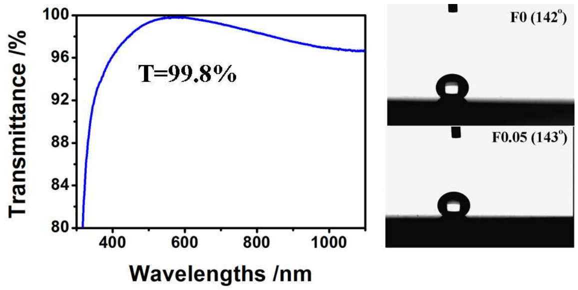

Environment-resistant fluoro-containing antireflective coatings was prepared by sol-gel process by co-condensation of tetraethylorthosilicate and 1*H*,1*H*,2*H*,2*H*-perfluoroalkyltriethoxysilanes (POTS).

Cite this: DOI: 10.1039/c0xx00000x

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Communications

Environment-resistant fluoro-containing antireflective coatings for high-powered laser system

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Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX
DOI: 10.1039/b000000x

A simple sol-gel route was proposed to prepare environment-resistant fluoro-containing antireflective (AR) coatings with nearly 100% transmittance by co-condensation of tetraethylorthosilicate and 1*H*,1*H*,2*H*,2*H*-perfluoroalkyltriethoxysilanes (POTS). These AR coatings can find great application in high-powered laser system.

High-powered laser system was designed to initiate the fusion reaction and gain a large amount of energy with no greenhouse gas emissions and less hazardous radioactive byproducts than current fission power plants. The most powerful high-powered laser system is the National Ignition Facility (NIF), which contains 7360 meter-scale optics including hundreds of transmissive optics.[1] The refractive indices of transmissive optics in NIF are 1.46-1.52. According to Fresnel equation, there will be about 8% reflection for each transmissive optic. Reflection on surface of hundreds of transmissive optics will seriously decrease the energy of lasers directed into the target which were used to initiate the fusion reaction. It is very helpful to suppress at maximum the reflection of the transmissive optics with antireflective (AR) coating.[1-2] The refractive index of sol-gel silica AR coating is equal to the square root of that of many common optical glasses, giving the coated glasses nearly 100% transmission.[3] In addition, the laser-induced damage threshold (LIDT) of sol-gel silica AR coating is two to three times higher than that of AR coatings from physical vapor deposition method. Therefore, sol-gel silica AR coatings have been widely used on transmissive optics in NIF.[4]

However, sol-gel silica AR coatings are hydrophilic and possess high specific surface areas, and therefore tend to adsorb contaminants, such as water or polar organic molecules (plasticizer of engineering materials in NIF), from the use environment.[5] The contaminants adsorbed into the pores of the AR coatings will degrade the optical property, which was known as poor environmental resistance of the hydrophilic silica AR coating. To overcome this problem, great efforts have been devoted to prepare ORMOSIL (organically modified silicate) AR coatings. In ORMOSIL AR coatings, there are amounts of organic hydrophobic groups, which can hinder the coating from adsorbing polar pollutants. The most common methods for preparation of ORMOSIL AR coatings are: (1) surface modification of AR coatings;[6-7] (2) co-condensation of tetraethylorthosilicate (TEOS) and hydrophobic silane precursors (e.g. methyltriethoxysilane (MTES) or dimethyldiethoxysilane (DDS));[8-9] (3) hybrid of silica with polymers.[10-11] However, to achieve satisfied environmental resistance, these methods need to add large amounts of polymer or hydrophobic silane precursors to give AR coatings enough hydrophobic groups. This affects the microstructure of silica clusters and the stacking texture of AR coatings, which reduces the transmittance.[9] In the NIF, the transmittance should be higher than 99.5%. 1*H*,1*H*,2*H*,2*H*-perfluoroalkyltriethoxysilanes (POTS) is a very effective hydrophobic modifier due to its low surface energy of perfloroalkyl chains.[12] In this work, we prepare environment-resistant fluoro-containing ORMOSIL AR coatings with nearly 100% transmittance by co-condensation of TEOS with a small amount of POTS.

TEOS, POTS, isopropanol, ammonia were added in a sealed glass container and then immediately stirred for 2 hours at 30 ℃. The formulas were shown in Table 1. The content of POTS was adjusted to give ORMOSIL sols with different fluorine content. The sols were named as S0, S0.005, S0.01, S0.02, S0.05 and S0.1 as the molar ratio of POTS to TEOS was 0, 0.005, 0.01, 0.02, 0.05 and 0.1, respectively. The sols were aged at 25 ℃ for 2 weeks before use. Finally, the silica sols were deposited on the well-cleaned BK-7 substrates by dip coating. The central wavelength of AR coating was adjusted to be about 500-600 nm by changing the withdraw rate during coating process. The AR coatings were heat treated at 80 ℃ for 2 hours under ambient atmosphere. The AR coatings were labeled as F0, F0.005, F0.01, F0.02, F0.05 and F0.1, respectively. More details about preparation of silica sols and AR coatings can refer to our previous work.[6, 10-11]

Table 1 The formulas of fluoro-free and fluoro-containing silica sols with isopropanol as dispersant

	TEOS /g	isopropanol /g	ammonia /g	POTS /g
S0-9.2	15.6	130	9.2	0
S0-4.6	15.6	130	4.6	0
S0	15.6	130	2.3	0
S0.005	15.6	130	2.3	0.23
S0.01	15.6	130	2.3	0.45
S0.02	15.6	130	2.3	0.90
S0.05	15.6	130	2.3	2.17
S0.1	15.6	130	2.3	4.15

Ethanol is the most common dispersant of silica sols in preparation of AR coatings. At the beginning, we also chose

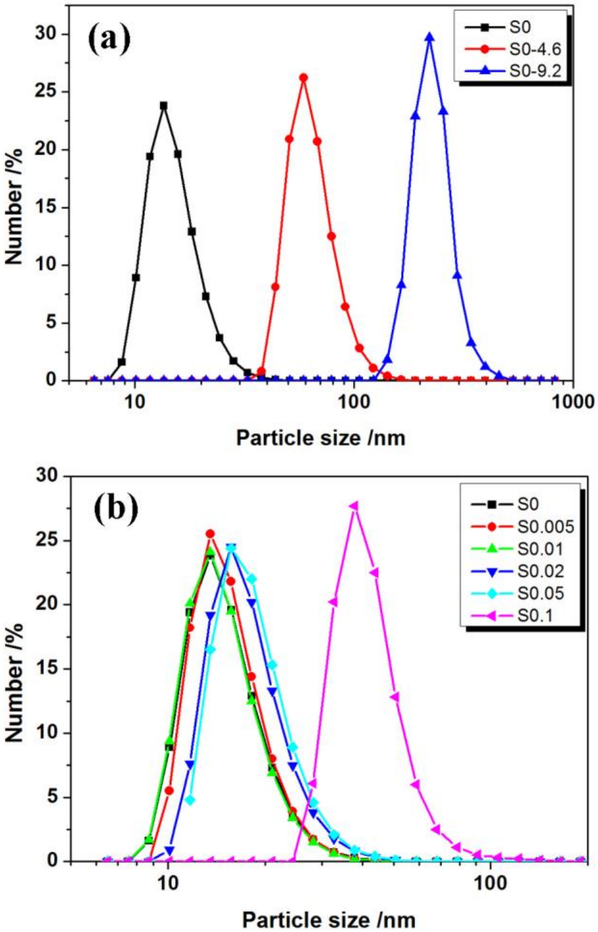

Figure 1 (a) Particle size of silica sols with different ammonia content (The mass of isopropanol and TEOS is 130 g and 15.6 g, while the mass of ammonia water is 2.3g, 4.6 g and 9.2 g for S0, S0-4.6 and S0-9.2); (b) Particle size of silica sols with different POTS content

ethanol as dispersant in preparation of fluoro-containing ORMOSIL sols. However, POTS is difficult to be dissolved in ethanol. There will be POTS oil drops at the bottom of glass container. After being aged for several days, the insoluble POTS drops turned into precipitate. This indicated that little POTS had been incorporated into silica particles by co-condensation of TEOS and POTS. Therefore, a good solvent of POTS must be used as new dispersant in preparation of fluoro-containing ORMOSIL sols.

Isopropanol can dissolve POTS well and hence was used as dispersant in this work. Therefore, in this work, a new formula was optimized for preparation of silica AR coating with isopropanol as dispersant. To obtain silica AR coating with nearly 100% transmittance, the particle size of silica particles should be about 20 nm.[3] The particle size of silica particles from Stöber method can be conveniently controlled by adjusting the ammonia content.[13] Figure 1(a) shows the particle size of silica sols with different ammonia content. By decreasing ammonia content from 9.2 g to 2.3 g, the particle size of silica sols decreased from 254 nm to 15 nm. Thin films from S0, S0-4.6 and S0-9.2 were coated to test their refractive index. However, thin film from S0-9.2 was difficult to realize. Therefore, only the refractive index of thin films from S0 and S0-4.6 were tested and shown in Figure 2. As

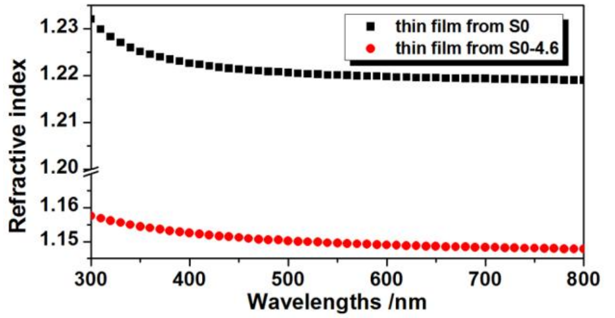

Figure 2 Refractive index dispersion curve of thin films from S0 and S0-4.6

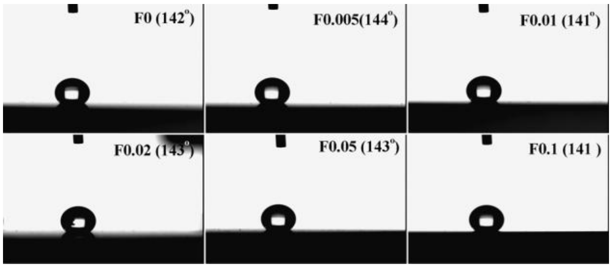

Figure 3 Water contact angles of AR coatings with different POTS content

shown in Figure 2, the refractive index of thin films from S0 and S0-4.6 at 550 nm is about 1.22 and 1.15, respectively. This means that thin film deposited by bigger particles possesses lower refractive index.[10] Besides, the refractive index of F0 (thin film from S0) is equal to the square root of that of substrate, and therefore it can be deduced that F0 would have nearly 100% transmittance. So, the ammonia content was set as 2.3 g.

Figure 1(b) shows the effect of POTS content on particle size. As shown in Figure 1(b), as the molar ratio of POTS to TEOS increased from 0 to 0.05, the particle size of silica sols increased very slightly from 15 nm to 18 nm. However, the particle size was almost tripled to 43 nm as the molar ratio of POTS to TEOS increased to 0.1.

Figure 3 shows the water contact angle images of AR coatings with different molar ratio of POTS to TEOS. It is a very interesting phenomenon that the water contact angle of F0, which is fluoro-free, is 142°. It is well known that inorganic silica AR coating from sol-gel method is totally hydrophilic because the surface of silica particles was covered by hydroxyl groups.[6,11] In this work, we replaced ethanol with isopropanol because POTS cannot be well dissolved in ethanol. Isopropanol was intended to be used as dispersant to dissolve POTS to obtain homogeneous fluoro-containing silica sols. However, the water contact angle result reveals that isopropanol might actively participate some reaction and replaced the -OH groups on surface of silica particles with -OCH(CH_3)$_2$. After silica particles being covered by hydrophobic -OCH(CH_3)$_2$ groups, the silica AR coating was almost superhydrophobic. The presence of -OCH(CH_3)$_2$ groups in silica particles was demonstrated by FTIR as shown in Figure 4. By increasing the molar ratio of POTS to TEOS from 0 to 0.1, the water contact angle almost remained unchanged. This is because the AR coatings have been almost superhydrophobic without POTS, it is very hard to further improve the hydrophobicity of AR coating.

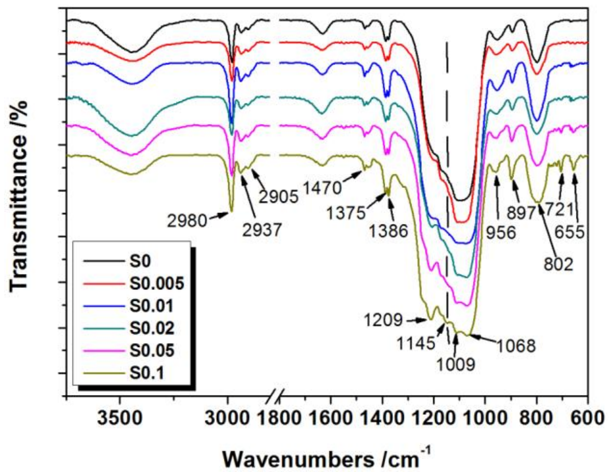

Figure 4 FTIR spectra of silica with different POTS content

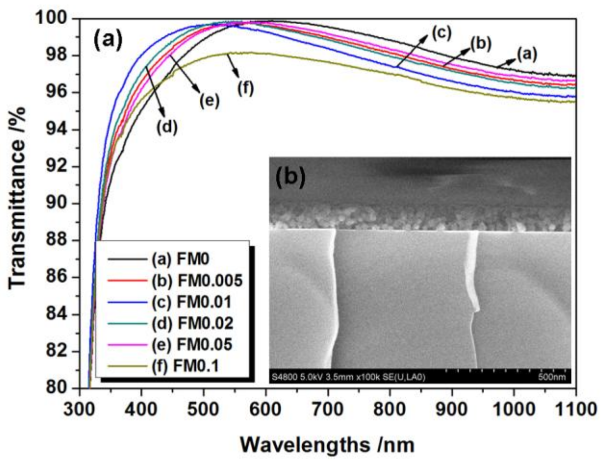

Figure 5 Transmittance spectra of AR coatings with different POTS content (a) and cross sectional SEM image of F0.05 (b)

The FTIR spectra of silica powders from silica sols with different POTS content were recorded with a Bruker Tensor 27 using KBr method in transmission mode. All silica were extracted exhaustively with isopropanol for 24 hours using Soxhlet apparatus, respectively, to remove the by-products from self-condensation of POTS. With ethanol as dispersant, the silica AR coating was hydrophilic.[6,11] Between 2000 cm^{-1} and 600 cm^{-1}, hydrophilic silica had only three absorption bands at 1068 cm^{-1}, 956 cm^{-1} and 802 cm^{-1} assigned to Si-O-Si and Si-OH.[10,14] However, with isopropanol as dispersant (S0 in Figure 4), there were four additional adsorption bands at about 1470 cm^{-1}, 1375 cm^{-1}, 1386 cm^{-1} and 897 cm^{-1}. Two absorption bands at 1375 cm^{-1} and 1386 cm^{-1} with same intensity were the very characteristic absorption bands for the $-CH(CH_3)_2$ groups. This demonstrated that the $-OCH(CH_3)_2$ groups were covalently bonded to the silica particles. In the spectra of fluoro-containing silica, further absorption bands assigned to C-F bond were revealed at 1209 cm^{-1} and 721 cm^{-1}.[15] These absorption bands increased gradually as the molar ratio of POTS to TEOS increased. The most important peak appeared at 1145 cm^{-1}.[16] These confirmed that the perfloroalkyl chains were clearly attached to silica particles.

Transmittance is the most fundamental property for AR coating. The transmittance of AR coatings used in high-powered laser system should be higher than 99.5%. Figure 5 (a) shows the

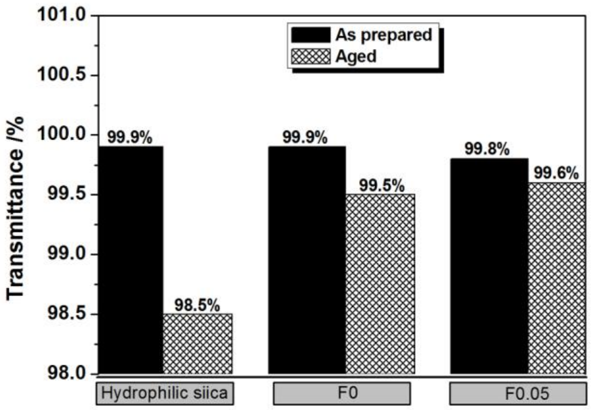

Figure 6 Environment-resistance of F0 and F0.05 AR coatings to hydrophilic and hydrophobic pollutants

transmittance spectra of AR coatings with different POTS content. The transmittance of AR coating was unchanged to be nearly 100% while the molar ratio of POTS to TEOS increases from 0 to 0.05. Silica AR coatings from sol-gel stöber method are consisted of a layer of silica particles which stack randomly on substrate. The refractive index of dense silica thin film is about 1.46. With appropriate particle size, the pores between silica particles lower the refractive index porous silica thin films to the square root of that of substrate, and hence the silica thin films would possess nearly 100% transmittance. As shown in Figure 5(b), F0.05 is a porous thin film stacked by silica particles. As the molar ratio of POTS to TEOS increased to 0.1, the transmittance decreased to 98.2%. The particle size of S0.1 is three times as that of S0.05. The big particles result in low refractive index.[10] The refractive index of AR coating for NIF should be about 1.22 to give 100% transmittance. The deviation of refractive index of F0.1 from the optimal value obviously decreased the transmittance. Besides, the big particles also lead to light scattering on coating's surface.

The environmental resistance of AR coating in high-powered laser system is very important. Hydrophilic silica AR coating has poor environmental resistance. As shown in Figure 6, by exposing to humid environment (about 95% humidity) for 2 month, the transmittance of hydrophilic silica AR coating, which was prepared from silica sol with ethanol as dispersant, decreases obviously from 99.9% to 98.5%. However, the transmittance of F0 and F0.05 decreased only from 99.9% to 99.5% and 99.8% to 99.6%, respectively. This indicates that both fluoro-free and fluoro-containing silica AR coatings possess good environmental resistance. This is an unexpected result. At the beginning, we believed that F0 would have poor environmental resistance and the environmental resistance of AR coatings would be gradually improved with increasing POTS content. It is not clear whether POTS makes contribution to the environmental resistance.

In conclusion, a sol-gel process was proposed to prepared environment-resistant fluoro-containing AR coatings by using TEOS and POTS as co-precursor and isopropanol as dispersant. FTIR spectra results demonstrated that perfloroalkyl chains were covalently linked to silica particles. Although it is not clear whether POTS makes contribution to the environmental resistance, this work is still valuable. On the basis of this work, further research on amphiphobic property of fluoro-containing AR coatings will be carried out due to the very low surface energy of perfloroalkyl chains. The amphiphobic AR coatings would have environmental resistance to both hydrophobic and hydrophilic pollutants in high-powered laser system.

The authors gratefully acknowledge the support from Natural Science Foundation of China (31770535).

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