Support Information

A Convenient Sol-gel Approach to Prepare Nano-porous Silica Coatings with Very Low Refractive Indices

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Experimental Section

Preparation of the MTES/TEOS sols

The MTES/TEOS sols in this work were prepared by a modified classic Stöber method. [1] The precursors Methyltriethoxysilane (MTES) and Tetraethoxysilane (TEOS) were purchased from Alfa Aesar (China) Chemical Co., Ltd., and distilled four times before use. Anhydrous ethanol (EtOH) was used as solvent and aqueous ammonia (13.4 mol/L) as catalyst. These reagents were successfully added into a glass bottle, and then stirred at 30℃ for 2 h. The final molar ratio of Si (total amount of MTES and TEOS): H_2O: EtOH: NH_3 is 1: 3.25: 37.6: 0.17, and sols with molar ratio of MTES/TEOS ranged from 0-3.0 were prepared. For different molar ratio of MTES/TEOS, the total amount of Si remains the same. After two hours of stirring, the sols were aged at 25℃ in the sealed bottles for 20 days. Before deposition, the sols with MTES/TEOS ranged from 0.1 to 3.0 were diluted with equal amount of anhydrous ethanol.

Fabrication of single-layer quarter wave coatings

The fused silica glass (rounded, with Φ= 30 mm, *d*= 2 mm and refractive index *n*= 1.457) were used as substrates, and thoroughly cleaned before deposition. In the process of dip-coating, different withdrawal rates were applied to achieve suitable film thickness[2] so as to set the reference wavelength around 632.8 nm, in accordance with the wavelength of the incidence light in ellipsometry measurement. Finally these coatings were treated at 160℃ for 4 h under air ambient.

Preparation of xerogels

The xerogels were obtained from the corresponding MTES/TEOS sols by volatilizing the solvent at 160℃ under air ambient, the same condition of establishing coatings. After the solvent evaporated, the crude xerogels were extracted exhaustively with ethanol for 24 h using Soxhlet apparatus to remove any possible residual reactors and byproducts. Finally, the extracted xerogels were heat-treated again at 160℃ to achieve the product powders.

Characterization of Optical and Physical properties of product coatings

The refractive indicies *n* of these coatings were measured on the ellipsometry (SENTECH SE850, Germany) at λ= 632.8 nm using a He-Ne laser as the light source. Transmission spectra were measured with an UV-Vis spectrophotometer (Mapada, UV-3100PC, China). The nitrogen adsorption/desorption isotherms of the corresponding xerogels were detected on a BET equipment (Autosorb SI, Quanachrome, USA) and the multi-point BET method was applied to determine the pore size, pore distribution and pore volume. The scanning electrons microscope (SEM, JSM-5900LV, JEOL) was used to take the surface morphologies of product coatings, and images of sol particles were obtained by the transmission electron microscope (TEM, JEM-100CX, JEOL). The FT-IR spectra of several xerogels were measured with a spectrometer Tensor 27 (Bruker, Germany) using KBr method in

transmission mode, and the water contact angles of coatings were received from an optical contact angle measuring instrument (DSA100, Krüss, Germany).

Supplementary Results

The BET data of several represent exrogels

The pore size, pore volume and pore size distribution were listed in Table S2 and Fig. S1, respectively. Sol particles with small pore size and acute distribution, that is pivotal to obtain a coating with excellent transmittance. It is well known that the refractive indices of nano-porous materials depend on the porosity, as reported by B. E. Yoldas in 1980:[3]

$$n_\rho^2 = (n_b^2 - 1)(1-\rho) + 1 \qquad (1)$$

where ρ is the porosity of nano-porous materials, n_b is the refractive index of the related bulk materials, and n_ρ is the effective refractive index of nano-porous materials. In the present work, the porosities of the coatings were estimated from the pore volumes measured by the BET measurements, and these porosities values were then substituted into Equation (1) to obtain an approximate refractive index of our product coatings.

Table S1 The deduced porosity and refractive index *n*

Sample (xerogels or coatings)	Measured BET data		Data Deduced		Measured *n* (at 632.8 nm)
	Pore size (nm)	Pore volume (cc/g)	Porosity ρ	n_ρ	
MTES/TEOS=0	2.366	0.7308	62.80%	1.191	1.211
MTES/TEOS=0.1	2.857	0.7996	64.88%	1.181	1.175
MTES/TEOS=0.8	3.964	1.280	74.73%	1.133	1.127
MTES/TEOS=1.5	4.063	1.249	74.26%	1.135	1.106
MTES/TEOS=3.0	3.108	0.7942	64.72%	1.182	1.104

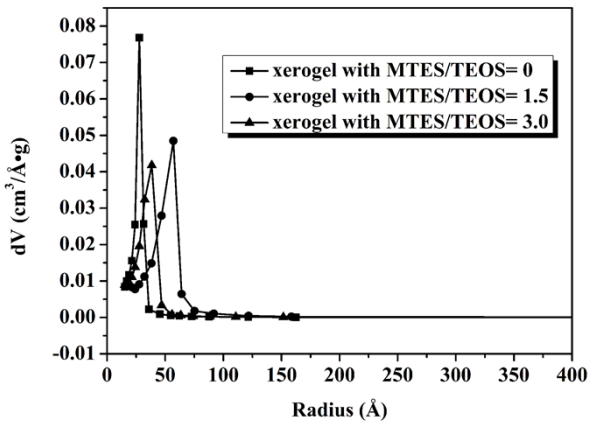

Fig. S1 The pore size distribution of the presented xerogels

In the calculation, following assumptions have been adopted: (1) The xerogels or the product coatings are composed of SiO_2 (-O-Si-O-) only, noting that -Si-CH_3 incorporated by MTES can be approximately considered as -Si-O- since the relative molecular mass of -CH_3 is similar to that of -O- ; then (2) the xerogels and the product coatings can be regarded as different forms that comprise bulk silica (n= 1.457) and pores (n≈ 1.0); thus (3) for a certain amount of xerogels or coatings, their weight was contributed almost by bulk silica, while the relatively large volume was maintained by the introduced pores. In addition, the density of bulk silica is aroud 2.31 g/ml as recorded. Thereafter, we can take the pore volume of the xerogel with MTES/TEOS= 0 as an example, to show the deducing process as follows:

(1) The physical meaning of pore volume 0.7308 cc/g is, the volume of pores in 1 g porous xerogel V_{pore}= 0.7308 ml;

(2) The volume of 1 g bulk silica V_{bulk}= 1 g÷ 2.31 g/ml= 0.4329 ml;

(3) The total volume of 1 g porous xerogel $V_{total}= V_{pore}+ V_{bulk}$= 0.7308 ml+ 0.4329 ml= 1.1637 ml;

(4) The approximate porosity of the corresponding coatings (in fact, the porosity of the porous xerogel) ρ= 0.7308 ml÷ 1.1637 ml× 100%= 62.80%;

(5) Substituted this ρ into Equation (1), and finally obtain an approximate effective refractive index of the product coating n_ρ= 1.191.

Employing the same process, the porosity and the approximate refractive index of other coatings with different ratio of MTES/TEOS can be calculated, and the deduced values are listed in Table S2 as well as the measured data from ellipsometry.

IR spectra of xerogels and contact angles on the coating-water interface

Fig. S2 shows the IR spectra of the xerogels with different ratio of MTES/TEOS. As seen, the adsorbing band at 1095 cm^{-1} is attributed to the asymmetric stretching vibration of the Si-O-Si group, the main framework of nano-porous silica xerogels and coatings. Notably, new adsorbing band emerged along with the use of MTES, corresponding to the symmetric deformation of C-H bonds in the Si-CH_3 group. This confirmed the incorporation of methyl groups by MTES. Furthermore, methyls were known as hydrophobic groups with low polarity, and would rouse an increasing of contact angles on the coating-water interface when they were embedded in coatings. As shown in Fig. S3, the increased contact angles with the increase of MTES/TEOS ratio, indicates the existence of methyl groups in MTES/TEOS coatings.

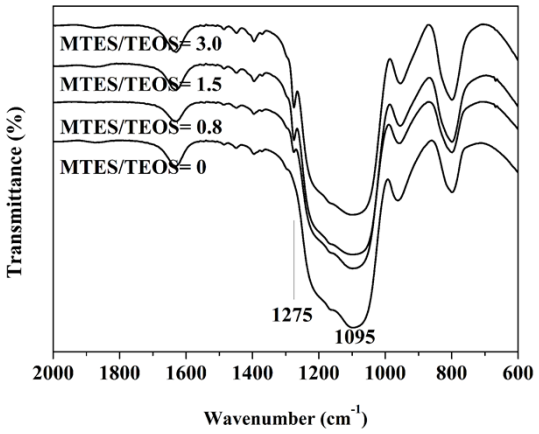

Fig. S2 The IR spectra of silica xerogels with different ratio of MTES/TEOS

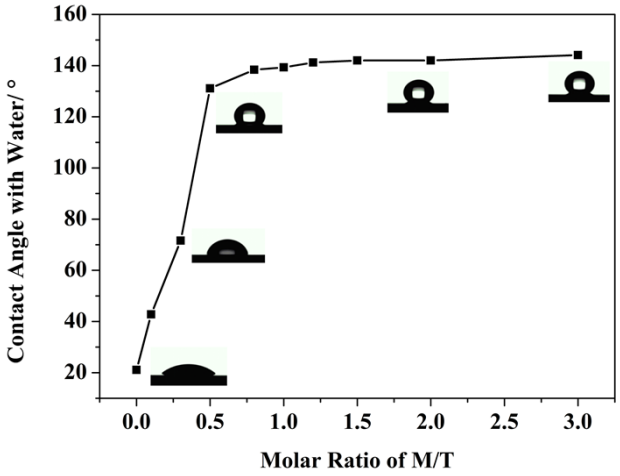

Fig. S3 The water contact angles with nano-porous coatings with different MTES/TEOS

References

1 W. Stöber, A. Fink and E. Bohn, *Journal of Colloidal and Interface Science*, 1968, **26**, 62;

2 L. J. Crawford and N. R. Edmonds, *Thin Solid Films*, 2006, **515**, 907;

3 B. E. Yoldas, *Applied Optics*, 1980, **19**, 1425.