



Cite this: *Chem. Commun.*, 2014, 50, 13813

Received 13th July 2014,
Accepted 15th September 2014

DOI: 10.1039/c4cc05397d

www.rsc.org/chemcomm

A convenient sol–gel approach to the preparation of nano-porous silica coatings with very low refractive indices†

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Silica coatings with refractive indices as low as 1.10 were prepared via a one-step base-catalysed sol–gel process using methyltriethoxysilane and tetraethoxysilane as co-precursors. No expensive equipment was required and the method did not require etching or high-temperature calcination.

The refractive index contrast is an important figure of merit for distributed Bragg reflectors,¹ optical microresonators and broadband antireflective coatings in ambient air.^{2,3} However, the realization of practical devices with excellent optical properties has been hindered by the current lack of optical materials with very low refractive indices (n), especially those that closely match the refractive index of air. This has motivated the development of novel materials with refractive indices lower than those of conventional optically transparent materials.^{4–6} Silica (SiO₂) and magnesium fluoride, with refractive indices of 1.46 and 1.39, respectively, have the lowest practical refractive indices that can be achieved in dense materials. Nano-porous SiO₂, with a refractive index of 1.23, has been widely used as a quarter-wave layer.^{7,8} However, even nano-porous SiO₂ does not satisfy the requirement for a material with a refractive index close to that of air ($n_a = 1.0$).

Numerous investigations have been carried out to develop materials with an ultra-low refractive index. Chemical etching was one of the earliest techniques and is now one of the most commonly used methods; materials with $n = 1.14$ and even $n = 1.07$ have been obtained *via* etching.^{9,10} However, the use of highly hazardous acid etchants is a disadvantage in large-scale applications. Approaches based on the phase separation of polymers or burning off additional templates have been demonstrated to be

effective in obtaining nano-porous layers,^{11,12} but the use of environmentally hazardous solvents or high calcination temperatures is undesirable for certain polymer substrates. Xi and co-workers^{3,13} reported two silica nano-rod array films for broadband antireflective coatings with refractive indices as low as 1.08 and 1.05. These coatings were prepared *via* oblique-angle deposition, an expensive process that cannot be used to tune the refractive index and film thickness and is also unsuitable for large substrates.

It is well known that the sol–gel process is a potential method for the preparation of nano-porous materials as a result of its low process temperature, low cost, the high purity of the resulting materials and the availability of substrates with complex shapes.¹⁴ We report here a simple procedure to prepare nano-porous silica films with a very low refractive index by dip-coating deposition *via* a one-step base-catalysed sol–gel process. Methyltriethoxysilane (MTES, Alfa Aesar) and tetraethoxysilane (TEOS, Alfa Aesar) were used as co-precursors. These compounds were hydrolysed and co-condensed in an ethanol solvent with an aqueous ammonia catalyst to build aged sols for deposition as coatings. The product coatings were established after heat treatment at 160 °C under ambient air without the need for expensive equipment, an etching process, the addition of polymers or templates for further phase separation, or calcination at high temperatures (for experimental details, see the ESI†).

Fig. 1a shows the refractive index of the resultant silica coatings *versus* the molar ratio of MTES/TEOS in the sols measured by ellipsometry (SENTECH SE850 UV, Germany) using a He–Ne laser as the light source ($\lambda = 632.8$ nm). The coatings derived from the pure base-catalysed sol with MTES/TEOS = 0, *i.e.* with TEOS as the single precursor, had a low refractive index of 1.21, in good agreement with previously reported results.^{7,8} With increases in the MTES/TEOS ratio, the refractive index n decreased rapidly at first, then slowed down and approached a stable and ultra-low value ($n = 1.10$). As all the measured coatings have been designed as quarter-wave coatings, *i.e.* with a thickness equivalent to one-quarter of the wavelength of the incident light, their transmittance can be

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† Electronic supplementary information (ESI) available: Experimental details, BET data analysis and the deducing details of calculated porosity, IR and contact angle analysis. See DOI: 10.1039/c4cc05397d

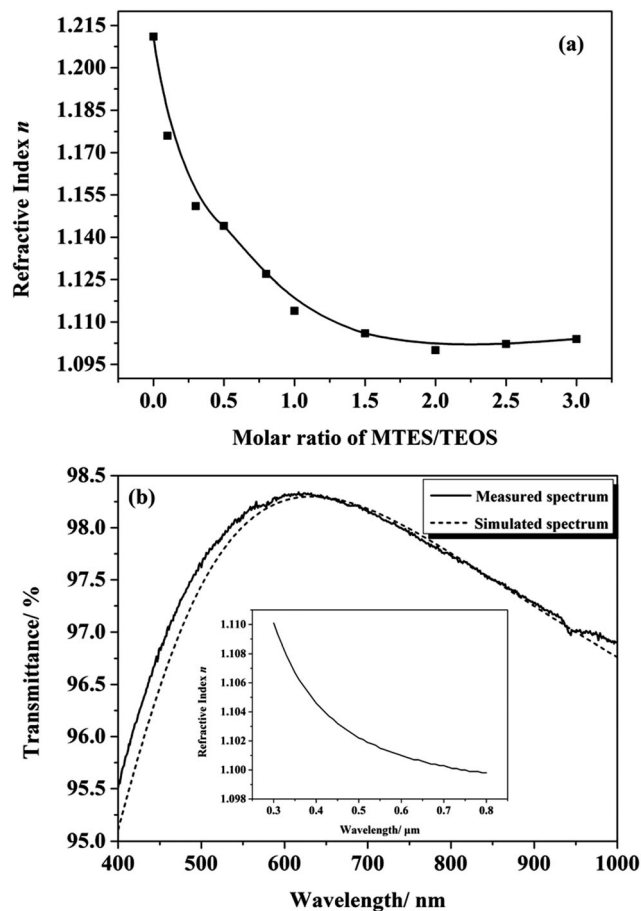


Fig. 1 (a) Refractive index of the base-catalysed MTES/TEOS coatings and (b) the measured transmittance spectrum of coatings with MTES/TEOS = 2.0 (solid line) and the simulated spectrum from software for the design of thin films (TFCalc, Version 3.5, Software Spectra Inc., USA) with $n = 1.10$ by setting the reference wavelength at 632.8 nm. Good agreement between the experimental and simulated curves is further evidence that these nano-porous silica coatings have a very low refractive index of 1.10. Inset shows the dispersion curve of the corresponding coatings in (b).

used to evaluate the optical properties of the coatings according to the simplified Fresnel formula.¹⁵ Fig. 1b shows the measured transmittance spectrum of coatings derived from the sol with MTES/TEOS = 2.0 and the simulated spectrum from software for the design of thin films (TFCalc, Version 3.5, Software Spectra Inc., USA) with $n = 1.10$ by setting the reference wavelength at 632.8 nm. Good agreement between the experimental and simulated curves is further evidence that these nano-porous silica coatings have a very low refractive index of 1.10.

These reported coatings consist of a layer of silica particles randomly stacked on the optical substrates; the effective refractive index of these nano-porous coatings can be estimated by their porosity.¹⁵ The porosity of the coatings results from (i) the pores created during the stacking of the particles and (ii) the pores inside the particles. We used BET to estimate the porosity of the coatings as this is a convenient method of determining the pore size, pore size distribution and pore volume of a solid powder. Xerogels were prepared from the corresponding MTES/TEOS sols by volatilizing the solvent at 160 °C, extracting with ethanol and then testing on the BET equipment (Autosorb SI, Quantachrome, USA). The BET measurement results are given in Table S1 and Fig. S1 (ESI†).

The pore size was in the range 2–4 nm, much smaller than the wavelength of light, and the size distributions were narrow, so there was no light scattering. In addition, the pore volume was used to evaluate the porosity of the coatings and the effective refractive index of the coating was calculated from this porosity value (see ESI†). Table S1 (ESI†) shows that the calculated and measured refractive index values of the coatings were comparable when the MTES/TEOS ratio was <0.8 ; however, the deviations between the calculated and measured refractive indices were greater at higher MTES/TEOS ratios. The main reason for this discrepancy is the difference in the structural pattern of the xerogels and coatings. Part of the stacking porosity in the coatings may not exist in the xerogels. The proportion of this porosity that disappeared became more important with increases in the MTES/TEOS ratio, which may result in a greater difference between the calculated and measured values of the refractive index. The porosity inside the particles reaches a maximum value at a certain point as the MTES/TEOS ratio increases; further decreases in the measured refractive index are probably due to the increasing stacking inter-particle porosity. Fig. 2 shows the surface images of the coatings obtained by SEM (JEOL JSM-5900LV). These images qualitatively demonstrate that the stacking porosity increases from the pure base-catalysed coatings with MTES/TEOS = 0 to the coatings with MTES/TEOS = 3.0.

Gelation occurs on the substrates during the dip-deposition process and the following heat treatment; the colloidal particles link together to form a three-dimensional network. The physical characteristics of the gel network, *i.e.* the coating, depend on the extent of cross-linking before gelation.¹⁶ When the methyl groups were incorporated into the silica network with MTES, the Si–OH groups were partially substituted by Si–CH₃ (Fig. S2 and S3, ESI†), resulting in a decrease in the polarity of the silica particles. Consequently, the intermolecular forces, in particular the hydrogen bonds among these methyl-embedded particles, were weakened and the extent of cross-linking after the final heat treatment was greatly reduced, leading to a relatively high stacking density (Fig. 2).

Fig. 2 not only demonstrates the change in stacking porosity, but also that in the morphology of the silica network with different ratios of MTES/TEOS. With low values of MTES/TEOS, the coatings are built from independent silica particles, which can be clearly distinguished in Fig. 2a and b. As the ratio of MTES/TEOS increases, the discrete silica particles are gradually substituted by particle chains or sheets and the corresponding coatings show a quasi-honeycomb structure. This phenomenon originates from the morphology of the silica particles in the MTES/TEOS sols (Fig. 3, TEM images; JEOL JEM-100CX). The morphology of the different sol particles agrees with the stacking structure of the corresponding SEM images, which means that, with an increase in the MTES/TEOS ratio, the boundary of the silica particles gradually declines and particle chains or sheets form by the accumulation of silica particles with a low polarity. According to the controlled aggregation mechanism of Bogush and Zukoski,¹⁷ the particles in the sol grow by the aggregation of sub-particles; once the particles have reached a certain size, the sol attains a colloidal stability as a result of the surface charges.

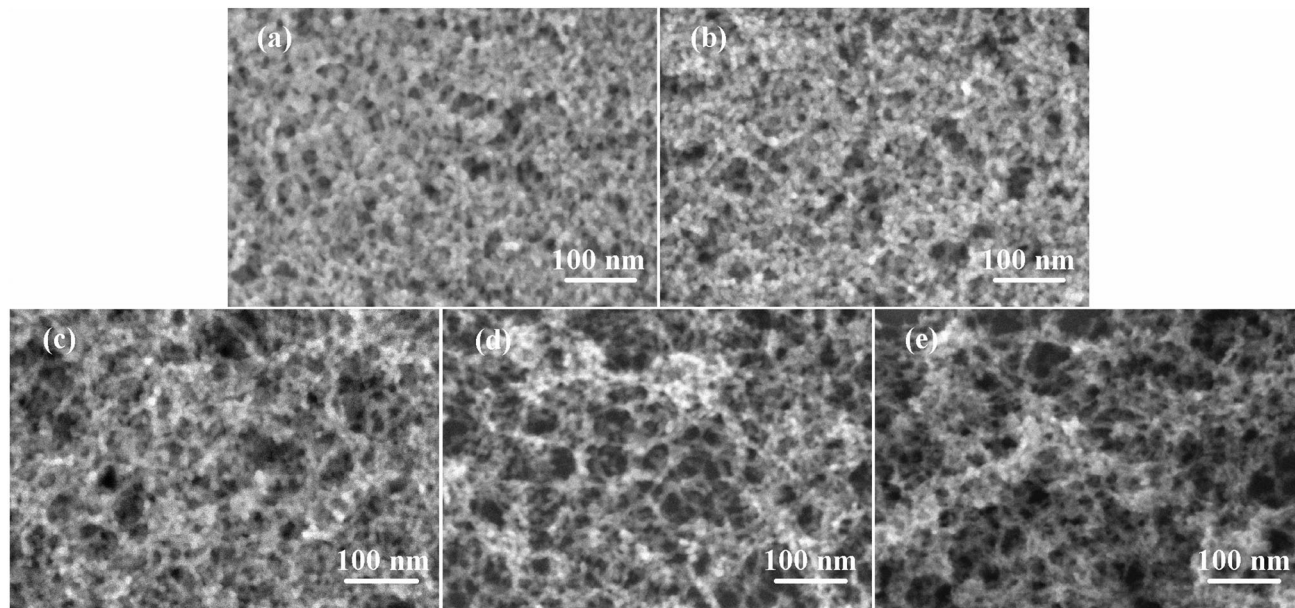


Fig. 2 SEM surface images of base-catalyzed silica coatings with (a) MTES/TEOS = 0, (b) MTES/TEOS = 0.1, (c) MTES/TEOS = 0.8, (d) MTES/TEOS = 1.5 and (e) MTES/TEOS = 3.0.

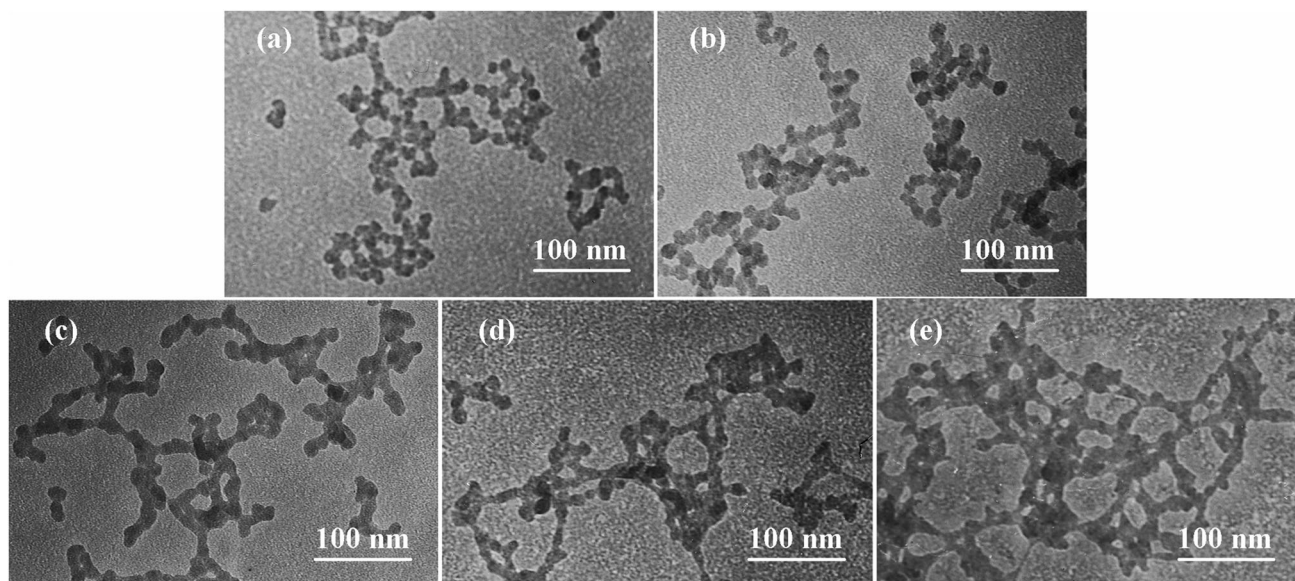


Fig. 3 TEM images of sol particles with (a) MTES/TEOS = 0, (b) MTES/TEOS = 0.1, (c) MTES/TEOS = 0.8, (d) MTES/TEOS = 1.5 and (e) MTES/TEOS = 3.0.

In the work reported here, the incorporation of methyl groups on silica particles by MTES disturbs and retards the charge balance, leading to an increase in the sol particle size (Fig. 2a–c). The effect of the steric hindrance of these methyl groups enlarges the pore size in the silica particles, as confirmed by the BET data in Table S1 (ESI[†]). However, when the MTES/TEOS ratio reaches a certain point, the existence of abundant methyl groups on the surface of the sub-particles means that steric hindrance becomes the dominant factor, which may terminate the aggregation of sub-particles in one particle at an earlier stage; this results in a relatively small particle size. In addition, the excess methyl

groups take up space in the pores, explaining the observation that the pore size of the xerogel with MTES/TEOS = 3.0 deviates from the increasing trend in Table S1 (ESI[†]).

In conclusion, a convenient procedure is proposed to fabricate coating materials with very low refractive indices. Nano-porous silica coatings with refractive indices in the range 1.21–1.10 can be produced *via* this one-step base-catalysed sol-gel process using MTES and TEOS as co-precursors. This approach is a promising alternative to fabricating coating materials with a very low refractive index and may find potential applications in fields of opto- and microelectronics.

The authors gratefully acknowledge the support from China National Petroleum and Gas Corporation Science and Technology Development Project “Nano intelligent chemical agent” (2011A-1001).

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