Supporting Information

Gradient Inverse Opal Photonic Crystals via Spatially Controlled Template Replication of Self-Assembled Opals

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Atomic layer deposition

Custom designed stop–flow type of ALD reactor was used to perform the depositions at 70 ^{o}C. Titanium tetrachloride at 99.999% purity obtained from Sigma Aldrich and deionized water were used as precursors for TiO_2 deposition. Precursor vapor delivery system was designed to accurately control the precursor gas flow rate and exposure during the infiltration of the opal. LabVIEW based programming software was developed for recording and controlling varying precursor exposures for gradient atomic layer deposition process. For gradient depositions, precursor exposures of titanium tetrachloride were decreased linearly with number of cycles from the initial exposure value to the lowest possible exposure control (0.2 mbar sec). ALD was operated in stop–flow process (fill–hold–purge method).[1] The pulse step of traditional continuous flow process is divided into fill and hold where the precursor gases were filled up to the set pressures and held for the set time at this pressure. Precursor exposure is calculated as the sum of the product of partial pressure and exposure time during fill and hold steps. The exposure for the water precursor was kept above the saturation exposure (120 mbar sec) in all the infiltration experiments.

Microstructural and Optical Characterizations

UV-VIS-NIR Cary 5000 spectrophotometer (from Varian Inc.) was used to measure transmittance data of the infiltrated opals. Field emission scanning electron microscopy (JEOL JSM 6340F) was used to obtain high-resolution microstructural images of the opal templates. Refractive index values for TiO_2 films were obtained from reflectivity and spectral ellipsometry measurements. Rutherford backscattering spectroscopy was used to measure the TiO_2 depth profile of infiltrated opals. A beam of 2.5 MeV H^+ ions was generated using the 3.5 MV HVE Singletron accelerator at the Centre for Ion Beam Applications, National University of Singapore, Singapore and was subsequently passed through a series of collimators.[2] Ions backscattered at 160° were measured with an ORTEC-Ultra Si surface-barrier detector, and a backscattering spectrum was collected for each sample.

Rutherford backscattering spectroscopy

Rutherford backscattering spectroscopy (RBS, using a 2 MeV proton beam) was employed to quantitatively evaluate the depth profile. Three infiltrated opal samples, namely uniformly infiltrated, Pt_{in} = 25 (lower magnitude of gradient) and Pt_{in} = 20 (higher magnitude of gradient) were selected to record their backscattering spectra as shown in Fig. S1. It can be clearly seen that Ti signal is different for all the three samples with highest backscattering yield found for uniformly infiltrated opal. Each spectrum was fitted using the SIMNRA simulation code to calculate the TiO_2 depth profile.[3] The areal thickness (in at/cm^2) of each layer from calculations was converted into an interim thickness for a solid layer, using the weighted average of the bulk densities for TiO_2 (4.26 g/cm^3) and C_8H_8 (1.06 g/cm^3). The interim thickness is the thickness of a solid layer of a TiO_2-C_8H_8 mixture. The approximate true thickness or depth was calculated from the interim thickness by including the void % to account for the empty space within each layer based on face centered cubic structure. As shown in Fig. S1, the Ti concentration remained constant for uniformly infiltrated opals within the depths determinable by RBS. For the gradient infiltrated opals, the Ti concentration decreased more sharply with depth for the sample with higher magnitude of gradient when compared to that with lower magnitude of gradient. A nonlinear Ti concentration gradient profile with depth can be observed. These results quantitatively confirm that the deposition gradients were smooth and controllable.

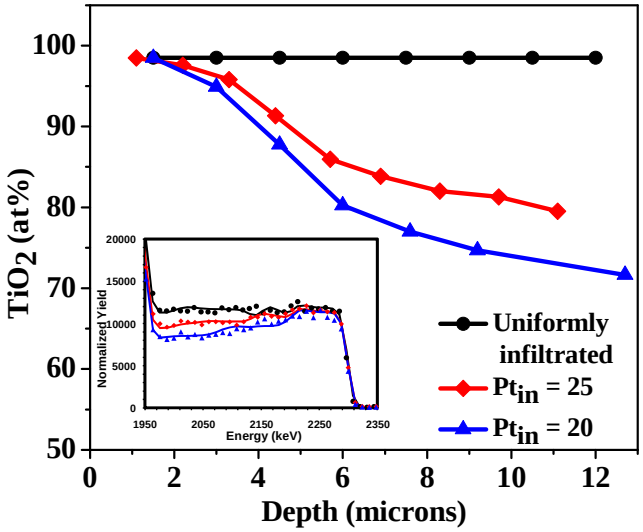

Fig. S1 Normalized TiO_2 depth profile calculated from RBS spectra (Inset: measured RBS spectra represented as dots along with obtained SIMNRA simulations in solid lines for the infiltrated opals)

References

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