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In situ synthesis of VO₂ for tunable mid-infrared photonic devices

J L Martinez Hurtado,^{*a} C Kraeh,^a A Popescu,^a H Hedler,^a and J J Finley^aReceived Date
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Photonic crystals are the perfect control units for manipulation of light due to their well-defined band-gaps. The geometry and optical properties of the materials define their light manipulation capabilities. In this work, a tunable photonic crystal is developed by synthesizing thermally controllable vanadium dioxide nanoparticles inside a photonic crystal array made of micrometrical hollow tubes. Through modulation of the phase transition and refractive index of VO₂, both bandwidth and position of the photonic bandgaps can be manipulated. We show the tunability and reconfigurability of these photonic crystals, paving the way to the realization of programable photonic devices.

1 Introduction

Photonic crystals (PhCs) are applied in a number of domains such as information processing, gas sensing, and telecommunications^{1–3}. It has been long investigated how to manipulate materials in such structures in order to induce changes in their photonic properties. In most cases the optical properties remain fixed after fabrication. This is a disadvantage since photonic properties also remain fixed for the particular fabrication and geometrical configuration. Small changes are sometimes required to dynamically match optical transmission characteristics, or for example guided mode frequencies in a waveguide, etc. Ideally, reversible and repeatable changes triggered by external stimuli (i.e. optically, electrically, magnetically, or thermally) would induce this changes for a particular application. A change in refractive index or dielectric constant is usually required to alter the photonic properties of these PhCs. Here, we show how this can be achieved practically by introducing a phase changing material in PhC structures designed for the mid-infrared.

Ferromagnetic polymers, hybrid nanoparticle-organics, liquid crystals, hybrid photochromic-inorganic materials, and a plethora of other inorganic substances^{4–18} are among the existing materials with tunable optical properties. The largest shifts in dielectric constant have been reported for vanadium dioxide (VO₂) due to its metal-insulator transition^{9,19,20}. VO₂ is the material of choice for large optical transitions upon thermal stimulus. The crystal phase of VO₂ changes from monoclinic to tetragonal when heated above its transition temperature of 68°C^{9,21}. It was recently re-

ported that this phase transition is stabilized by dynamics of the crystal lattice²². This phase changing ability is very attractive for applications such as smart windows, tunable coatings, fast optical switches, memories and transistors^{23–25}. It is possible to exploit this effect from VO₂ to control the properties of PhC devices as band structure calculations have shown using the VO₂ dielectric constant²⁶ transition. Other promising materials are hybrid organic-inorganic liquid crystals or photochromics that change with optical or electrical stimuli^{15,17}; or lanthanide composites that are sensitive to magnetic fields⁸. Here we demonstrate the incorporation vanadium dioxide in high aspect ratio microtube PhCs and their thermal tunability.

High aspect ratio hollow-rod arrays used in this work have been recently reported and fabricated²⁷. These crystal lattices are fabricated by filling high aspect ratio pores from Si wafers. The filling materials consist of thin oxynitride passivation layers, and a poly-Si layer which forms the tube walls²⁷. It was also demonstrated that by varying the wall thickness during fabrication it was possible to change their photonic properties in the mid-infrared²⁷. Therefore, these changes can be induced in real-time with a tunable material as demonstrated in this work. Example optical transmission spectra and SEM micrographs of such structures are presented in Figure 1A and 1B.

1.1 VO₂ incorporation in PhC.

Several calculations of the band structure using plane wave expansion methods (MPB) are shown in Figure 1C for a PhC with a radius to pitch ratio of 0.25 and a wall thickness of 300 nm^{27,28}. This calculation assumed complete filling of the microtube core and neglected the imaginary part of the refractive index. Figure 1C shows calculated band structures for temperatures below and above the transition temperature corresponding to $n=1.5$,

^{*} To whom correspondence should be addressed: leo.martinez@wsi.tum.de

^a Walter Schottky Institut, Technische Universität München, Am Coulombwall 4, Garching, Germany

^b Siemens AG, Corporate Technology, Otto-Hahn-Ring 6, D-81739, München, Germany

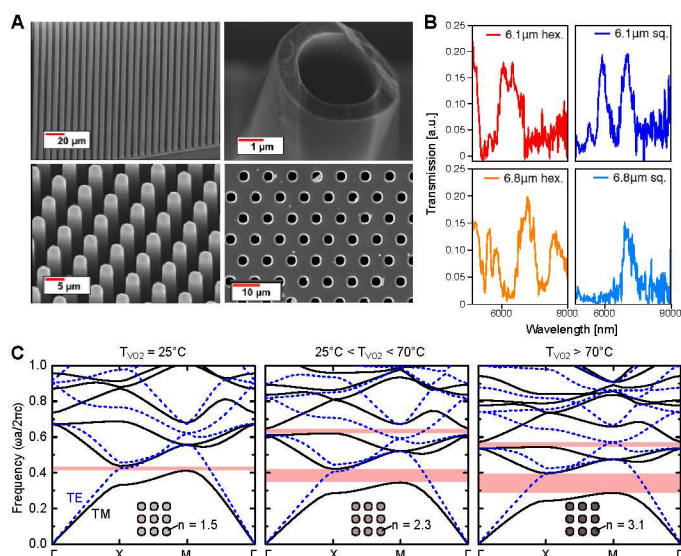
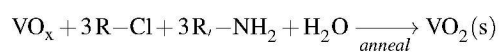
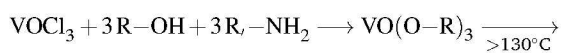


Fig. 1 Spectra, simulations and SEM micrographs of high aspect ratio PhCs. A) Scanning electron micrographs of square and hexagonal lattices showing their uniformity, high aspect ratio, hollow core, and bottom openings (reproduced with permission ©IOP Publishing)²⁷. B) Transmission spectra for square and hexagonal lattices with different pitch separation. C) Photonic band structure of a square microtube 6.5 μm lattice filled with an index varying material (VO₂). The refractive indices of the filling material correspond to: room temperature (25°C), a temperature above the transition temperature (70°C), and a temperature in between; shaded areas mark the TM band gaps.

$n=3.1$ and an intermediate stage corresponding to the change ($n=2.3$). A shift and widening of the photonic bandgaps are observed with increasing internal refractive index, thus, demonstrating the change of frequency and bandwidth of the photonic features by incorporating such materials. Although there are reported efforts in the literature for VO₂ implantation^{19,20}, the material selection and synthesis must be adapted for these high aspect ratio structures.

A common reaction for the VO₂ synthesis is based on the alkoxide chemistry of vanadium precursors. This reaction is well known and commonly used in industrial production of vanadium oxides²⁹. The mechanisms include a metal oxyhalide (MO_n-X_m) interacting with a primary alcohol (R-OH) to form the corresponding metal alkoxide (MO_n-(O-R)_m), and forming by-product haloalkanes (R-X) and other vapours³⁰. Vanadium oxychloride (VOCl₃) is often used as a precursor; vanadium-oxygen bonds are formed from the non-hydrolytic reaction with the primary alcohol and a primary amine (R-NH₂) is used for controlled crystal growth. The general reaction mechanism can be described as:



The vanadium oxides (VO_x) from the reaction mixture require thermal annealing to complete their crystal formation to VO₂, and to prevent further defects and oxidation. It was necessary

to adapt this general VO₂ synthesis reaction for its incorporation in PhC microtubes post-fabrication. The primary alcohol in the general reaction can be varied and is chosen accordingly to match reaction conditions, rheological properties, temperatures, by-products, particle quality, shape, etc. Low molecular weight alcohols are usually hydrated, thus not preferred for the synthesis as this may cause lower reaction efficiencies and higher content of undesired oxides. High molecular weight alcohols, on the other hand, have been reported for successfully controlling VO₂ nanoparticle formation. This so called sol-gel chemistry involves long chain organics (R ≥ 10 C atoms) and high temperatures for removing water and oxygen from the reaction mixture³¹, which in turn can lead to blockages of the tube entrances.

2 Experimental Section

2.1 Nanoparticle formation via sol-gel chemistry.

All reagents were purchased from Sigma-Aldrich unless specified; the methodology recites as follows: 7.9g of 1-octadecanol 95% and 31mL of oleylamine were mixed in a glass beaker while increasing the temperature to 130°C; then the temperature was kept constant for 1h at 130°C for degassing; subsequently, the solution was cooled down to 50°C and 4.5mL of vanadium (V) oxychloride 99% were added to the mixture (a portion of tungsten chloride could be added here for doping). Vanadium oxychloride is a very strong oxidizing agent that hydrolyzes in air producing fumes and amber stains in glassware, thus it must be rapidly transferred to the solution. Upon interaction with the octadecanol-oleylamine mixture, VOCl₃ turns black indicating the formation of vanadium alkoxides. Then, the solution was heated up to 250°C with a heating rate of 2°C/1min and kept at 250°C for 25min to allow the reaction to complete and by-products to evaporate; a glass stirrer was used through the process. At this point, nanoparticles were formed within the organic matrix limiting their growth and shape. As the mixture drops again to 50°C, the organic material thickens. In order to dissolve the organic material surrounding the nanoparticles, 45mL of a 1:2 toluene:methanol solution were added to the mixture. The organic material dissolved into a liquid phase at room temperature and was transferred in equal parts to plastic centrifugation tubes, and centrifuged at 6000rpm for 5min. The excess solution from centrifugation was decanted and the precipitated VO_x nanoparticles resuspended in 10mL hexane. Having the particles in solution is advantageous for their manipulation, however the presence of organics should be taken into account for the consequent annealing step. This colloidal suspension can be stored by flushing the vial with N₂ or used for incorporation into PhC devices.

2.2 Sample preparation for PhC filling and transmission experiments.

We used 2cm times 2cm square Si chips with different morphologies as depicted in Figure 2. Silicon chips with 1cm² 250μm depth wells as in Figure 2B were used to drop-cast or dip-cast VO₂ nanoparticle solutions for evaluation of their optical transmission characteristics. A transmission experiment was performed for this

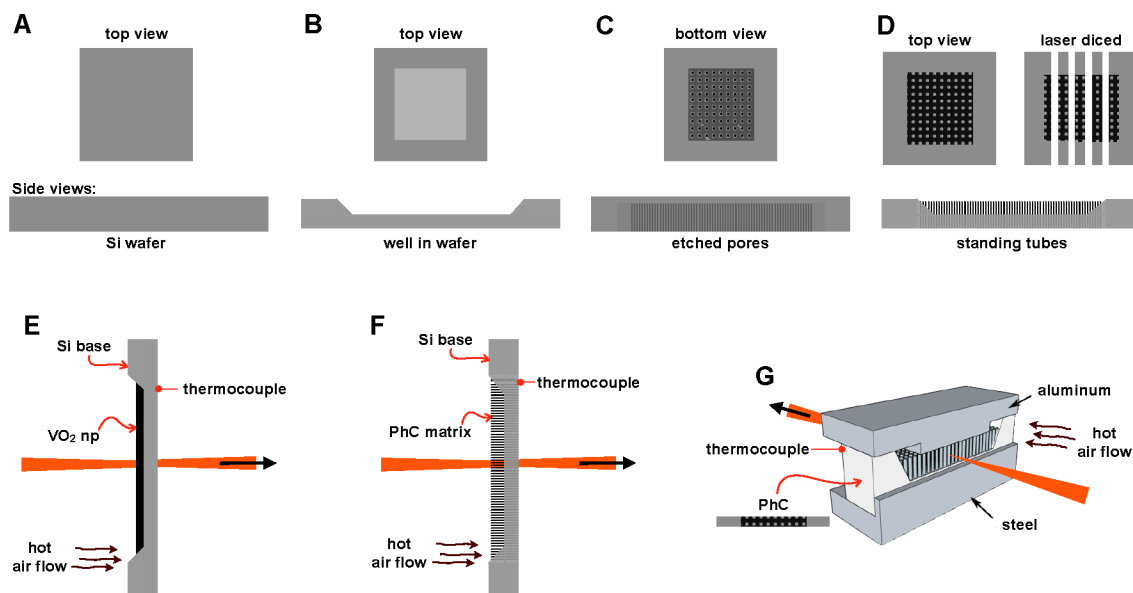


Fig. 2 Schematics of PhC sample preparation for transmission and microscopy experiments. A) Reference Si chip of 2cm by 2cm for comparison with the PhC samples. B) 250 μm deep wells etched in Si chip for transmission experiments of VO_2 nanoparticle suspensions. C) High aspect ratio pores etched from the bottom of the wafer for microscopy experiments. D) Fully fabricated PhC lattices similar to (C) but recessed from the back to expose the microtube tips; this samples were used for 2D grating transmission experiments, or sectioned in 1.5mm thin samples for transmission through the plane of periodicity. E) Transmission through the thickness of nanoparticles suspensions annealed in the wells from (B). F) Transmission from the bottom of the PhC lattice from (D) acting as a 2D grating. G) Transmission through the plane of periodicity in thin slices from (D) mounted in the sample holder.

purpose as illustrated in Figure 2E. Figure 2C depicts Si chips with etched pores with 6.7 μm square lattice that were used to evaluate the filling by optical and scanning electron microscopy. Finally, samples with standing microtubes as depicted in Figure 2D were used for transmission experiments, either as 2D gratings illuminating from the top as shown in Figure 2F, or as photonic crystals transmitting light through the plane of periodicity as shown in Figure 2G. The PhC geometry for the grating approach was a 12 μm square lattice with a 5 μm diameter and poly-Si wall thickness of 500 nm. For transmission through the plane of periodicity, the samples were 6.7 μm hexagonal lattice, 3 μm diameter, and 300nm wall. However, in this case the samples were sectioned into 1.5mm thin pieces with a laser cutter to preserve the PhC interface (532nm Nd:YAG, Figure 2D), and mounted in a metal sample holder specially designed for this purpose. The sample holder allows for effective light coupling by blocking the light from escaping above and below the sample with an aluminum lid and a steel base, and fixing the sample for transmission in the Γ -M direction accounting for \sim 250 microtubes transmission as depicted in Figure 2G.

2.3 VO_2 nanoparticles filling of PhC microtubes.

The nanoparticle suspension solutions dip-casted and drop-casted in the wells were annealed to complete the crystal formation from VO_x to VO_2 . The annealing step also ensures complete removal of any remaining organics by evaporation. The conditions were set to 450 $^\circ\text{C}$ annealing for 30min and ramping the temperature up over a 10s period under a 70mbar atmosphere (these conditions were limited by the annealing oven, shorter times and higher tem-

peratures can be used³¹). After the VO_2 phase transition was confirmed in the wells by temperature dependent transmission at 7.5 μm , the solution was drop-casted on the back surface of PhC samples with pores to evaluate filling via optical microscopy (Figure 2C). Alternatively, this samples were submerged in the nanoparticle suspension, sonicated and centrifuged to help the nanoparticle filling.

2.4 *In situ* formation of VO_2 nanoparticles in PhC microtubes.

Filling the microtubes requires special care for preserving the PhC intact. First, a circular mould was build on the back side of the PhCs resembling a pool to contain a fixed volume of liquid reagents. The mould consisted of a soft malleable adhesive made of synthetic rubber (Bostik UK) removable after synthesis. These samples were placed on top of a heating plate with the microtube tips facing the hot surface and the openings facing the liquid reagent reservoir. The reagents were transferred using a pasteur pipette and let to rest for 5min to ensure homogeneous pore filling. The temperature of the hot plate was raised to 150 $^\circ\text{C}$ resulting in \sim 130 $^\circ\text{C}$ on the PhC surface as corroborated with an IR thermometer. The heating rate was set to \sim 21 $^\circ\text{C}/\text{min}$ and the temperature was kept constant for 20min. The liquid darkened and vapours were produced leaving a fine black powder (VO_x). Finally, the samples were annealed at 500 $^\circ\text{C}$ for 5min by ramping up the temperature during 15s under a \sim 10mbar atmosphere (different annealing conditions can be used^{32,33}). Thin PhC sections (Figure 2D, diced), were filled by small droplets of the reagents solution carefully deposited on top of the PhC to

prevent leakage or damage of the PhC interface for effective light coupling; the droplets were held on top by the action of capillary forces. Optical and electron microscopy confirmed the presence, or absence, of VO₂ in the PhCs, which was then corroborated by light transmission experiments at different temperatures.

2.5 Mid-infrared transmission interrogation setup and temperature dependent experiments.

A custom built transmission set-up optimized for the mid-infrared was used to interrogate the samples (4.5-9 μm from a thermal light source)²⁸. The light was focused on front of the sample, and then onto a MCT detector spectrometer. A polarization filter was used to confine the mid-infrared light to the TM polarization with respect to the 2D photonic crystal (i.e. no E-field components in the photonic crystal plane). The setup was continuously flushed with nitrogen to remove excess humidity, which remained at a low level of RH < 11% as measured *in situ*. For temperature dependent transmission experiments, the sample holder was heated up with a hot air flow to ensure homogeneous heating of the microtubes. The temperature of the measured by the internal thermometer of the heat source and by a thermocouple attached to the back surface of the sample (Figure 2E-G). In order to prove the reversibility, repeatability and extent of the phase transition, heating and cooling cycles were performed at a fixed wavelength of 7.5 μm for the wells and 2D gratings, and at 5.2 μm for the transmission through the plane of periodicity.

3 Results and discussion

The three band diagrams in Figure 1C clearly show that the photonic band structure of the microtube PhC can be tuned by varying the refractive index of the filling material. Since the refractive index of VO₂ changes with temperature, it was possible to observe a similar tunability by applying heat, which in turn led to a shift of photonic bands to lower frequencies, and a decrease in transmission due to the metallic phase of VO₂.

Commercial VO₂ nanoparticles are scarce, thus they must be synthesized. Since their fabrication requires an annealing step to stabilize the VO₂ crystals, their incorporation into the microtubes was only possible prior to the annealing step. Long chain organics protect the crystal facets during growth^{30,34}, however they may be not suitable to fill microtubes. Here, a methodology similar to that from Paik *et al.*³¹ was used to synthesize VO₂ nanoparticles and fill in the high aspect ratio PhC microtubes. The presence of vanadium oxide particles was confirmed by light transmission experiments, which exhibit characteristic transmission decay as shown in Figure 3A. The presence of the particles was also corroborated by electron microscopy. This method resulted only in partial filling as shown in Figure 3B. Changes in the transmission intensity for large regions of the spectrum (5-9 μm) were observed, increasing for longer wavelengths, and agreeing with previously reported experiments⁹. A maximum shift was observed at 7.5 μm at which a temperature dependence experiment was recorded, as shown in Figure 3B, of the typical hysteresis for VO₂ phase transition at ~68 °C.

The synthesis was successful, however the filling by centrifu-

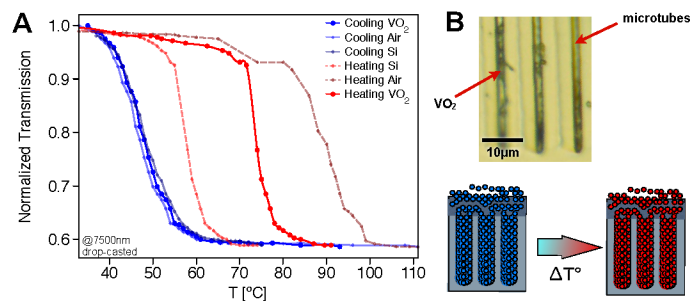


Fig. 3 Filling and transmission experiments with sol-gel synthesized VO₂ nanoparticles. A) Temperature dependent light transmission experiments at a fixed wavelength of 7.5 μm showing hysteresis of the VO₂ phase transition. The dashed line plots represent the temperatures recorded by the thermocouples in the heat gun and sample holder (blue when cooling, red when heating) to account for thermal differences. Solid lines represent the average temperature of the air and Si substrate, thus the assumed temperature for the VO₂. B) Optical microscopy of a cross section of a VO₂ filled sample by centrifugation showing incomplete filling.

gation or precipitation was not sufficient. Evaporation may have caused the air inside the tubes to expel material accumulated at the openings. Oleylamine and 1-octadecanol are very viscous at room temperatures, thus it is possible that the pores were blocked by bottleneck effects. Therefore, all further experiments used particles directly synthesized inside the microtubes. Figure 2 shows schematics of the microtube PhCs samples of Figure 1B used to evaluate the VO₂ pore filling and light transmission.

3.1 *In situ* formation of VO₂ particles in PhCs.

It was necessary to select reagents to ensure homogeneous filling. There are certain considerations that needed to be taken into account: since wavelengths in the mid-infrared region are larger than the microtube cross-section, particle homogeneity is not a strict requirement for transmission; and, as the growth will be limited by the diameter of the microtubes at the walls, controlling the particle size and shape is not necessary. Under this considerations, homogeneous nanoparticles are not required and any primary alcohol can be used in the synthesis according to the general reaction. Methanol, ethanol, iso-propanol, 1-butanol, 1-pentanol, and 1-hexanol were systematically used for VO₂ synthesis and filling of the PhCs. Since the primary amine stabilizes the nanoparticle growth by neutralizing reaction by-products²⁹, and the reaction of VOCl₃ from metal-alkoxides requires temperatures above its boiling point of 136 °C³¹, thus its presence can be precluded. This is a key factor for the simplification of the general reaction. Early works have reported VO₂ synthesis from the controlled vaporization of VOCl₃ onto crystal substrates at temperatures coinciding with its boiling point³³. Also, the synthesis of metal-alkoxides involves the production of haloalkanes (R-Cl) derived from the primary alcohol and the halogen in the VOCl₃. Therefore, using low molecular weight alcohols leads to low molecular weight haloalkanes which are volatile substances at such temperatures (e.g. 1-chlorohexane: 132 °C; chloromethane: -24.2 °C). Instant evaporation of these by-products is expected during the

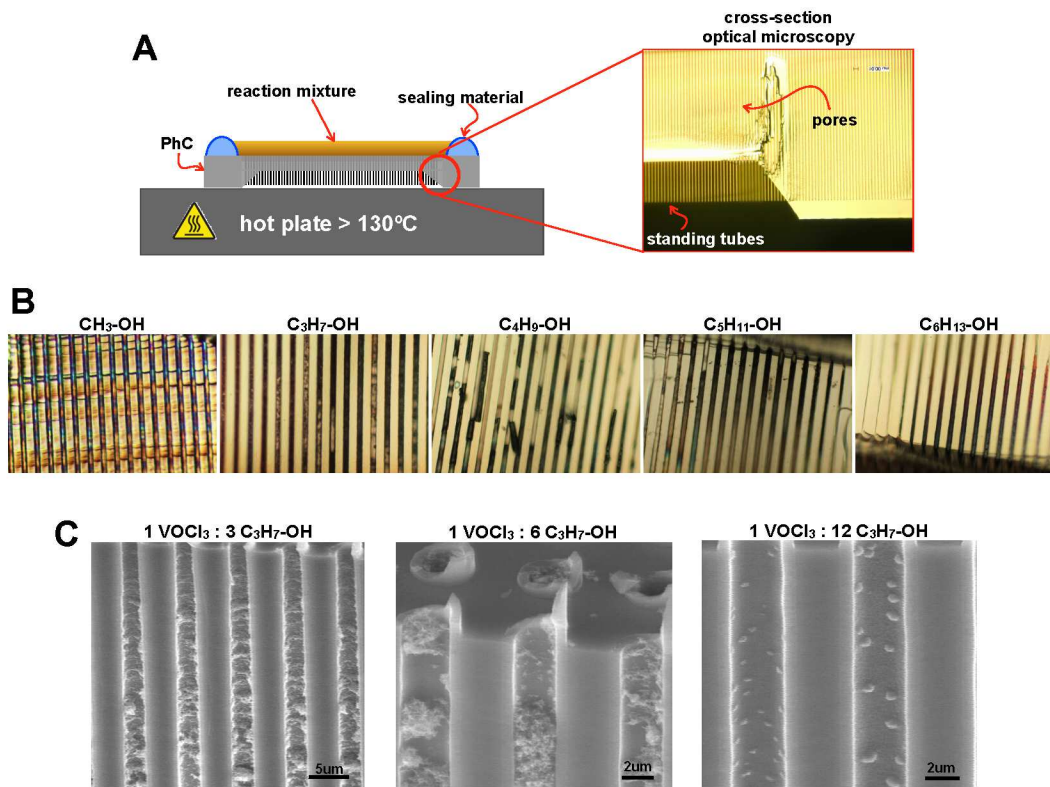
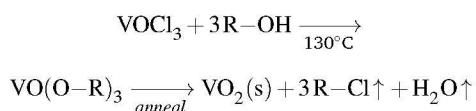


Fig. 4 *In situ* filling of PhC microtubes. A) Schematics of the reaction container and PhC sample showing the orientation of the microtube openings during the reaction. B) Optical microscopy of the resulting VO₂ in the PhCs filled with different alcohol precursors. C) Scanning electron microscopy of the resulting VO₂ in the PhCs by varying the excess amount of alcohol precursor.

reaction. Taking this into consideration, the general reaction can be simplified to:



We expected better yields from alcohols with boiling points near the one of VOCl₃, since low molecular weight alcohols may evaporate during the reaction. The filling may also be affected by the viscosity for higher molecular weights. The volume of the reagents was calculated using the molecular weights and densities given by the fabricant, and varying the molar ratio 1:1, 1:2, and 1:4 from the reaction stoichiometry for the different alcohol precursors tried. Typically, 0.2mL of VOCl₃ were added to the corresponding alcohol volume using a glass pipette. Times and temperatures can be adapted for optimized reaction conditions. The reaction reservoir is depicted in Figure 4A. All reaction conditions lead to successful synthesis of VO₂. Notwithstanding, some did not produce sufficient amount of filling or the same quality of VO₂ transition. Figure 4B shows optical micrographs of cross-sections of samples filled with the different alcohol precursors. Iso-propanol, butanol and pentanol gave the most promising results showing the largest amount of filling. The samples were sectioned with a diamond pen, the mechanical stress removed some material when breaking them. Having the alcohol reagent in excess did not improve the filling of the microtubes, however

resulted in different particle morphology and filling amounts as shown in Figure 4C. Since the aim of this work was to fill the microtubes, the alcohol-VOCl₃ ratio was fixed to 1:1 for the rest of the experiments and for all other alcohol precursors. Nevertheless, a detailed study of the reaction ratios for the different alcohols could allow for further optimization of this process in the future.

Annealing did not cause observable variations in the filling or morphology, thus only the evaporation of the reagents during the synthesis and the type of alcohol are the determining factors in the *in situ* synthesis. Transmission experiments corroborated these findings. Figure 5A shows a time dependent experiment for a sample placed in the grating direction (Fig. 2) at a fixed wavelength of 7.5μm. Pentanol produced VO₂ with the largest change in transmission followed by butanol and hexanol.

3.2 Transmission tunability in VO₂ filled PhCs

The VO₂ phase transition was checked by transmission through the crystal lattice of the PhCs acting as 2D gratings. Figure 5B shows transmission spectra for a PhC sample before and after filling and before and after heating, using isopropanol as precursor. A shift in the grating features occurs over the broad range measured, increasing from 60 to 70nm with a decay in transmission of 27%. These observations agree with the fact that VO₂ refractive index is larger for longer wavelengths with a maximum at ~17μm⁹. The effective refractive index change due to the

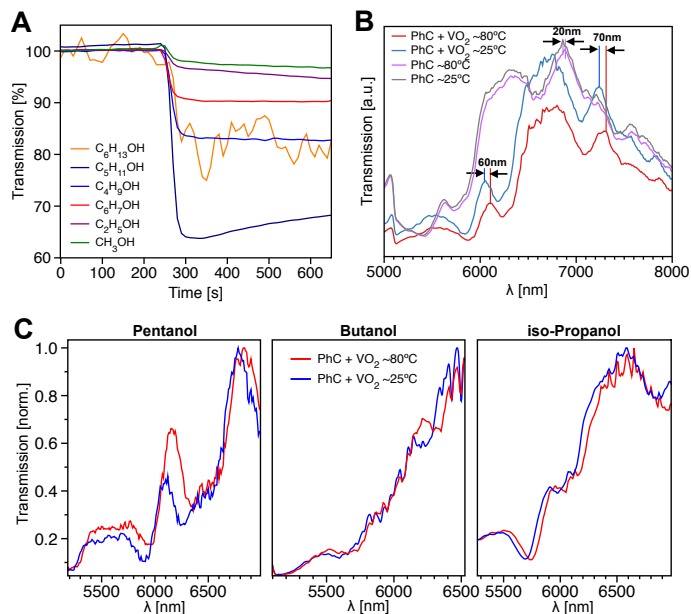


Fig. 5 Transmission experiments for PhC as 2D gratings. A) Transmission at a fixed wavelength of 750nm for microtubes filled with VO₂ synthesized from different alcohol precursors. The temperature was increased from 25°C to 80°C after 4min base line and kept constant for further 8min. B) Transmission spectra of a control sample without VO₂ and the same sample after *in situ* filling with VO₂, both before and after heating. The grating features are largely altered when filled and further modified when heating. C) Normalized transmission spectra before and after heating for *in situ* filled microtubes using different alcohol precursors.

phase transition affects overall the band structure and transmission features of the PhC as calculated in Figure 1C. We simulated those changes by considering the hollow geometry of the standing micro-tubes, which transmission shifts and decays as expected²⁸. Filling the tubes using other alcohol precursors led to shifts of similar magnitude in that wavelength range, as shown in Figure 5C. Pentanol was selected as the primary alcohol for all further experiments as it does not only fill the pores substantially, but also produces the largest changes in transmission. Pentanol has a boiling point above the reaction temperature and of the vanadium oxychloride, thus it evaporates only after the vanadium oxide crystal formation occurred.

In order to demonstrate that the VO₂ phase transition for tuning and reconfiguring photonic crystals, samples were prepared for transmission through the crystal plane of periodicity (Fig. 2). Transmission spectra were recorded at different temperatures showing the photonic crystal features shift along the Γ-M direction. The results are shown in Figure 6A. Figure 6C shows normalized spectra for the lowest and highest temperatures were a shift of ~100nm can be observed. This effect was found to be reversible and repeatable as shown in Figure 6B, it shows transmission at a fixed wavelength of 5.2μm for temperature of the sample modulated between 25°C and 55°C. Even at this short temperature range the changes are observed, proving that even small transitions in the crystal structure affect the light transmission. A 30°C change produced a transmission decay of 22%.

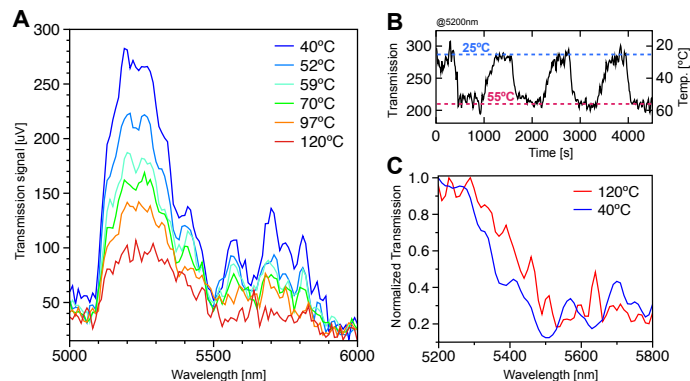


Fig. 6 Transmission experiments through the plane of periodicity for VO₂ filled hexagonal PhC. A) PhC transmission spectra at different temperatures showing a the photonic features change due to phase transition of VO₂. B) Transmission response at a fixed wavelength showing reversibility and repeatability of the VO₂ transition by slightly increasing the temperature. C) Normalized transmission for two temperatures showing the wavelength shift of the photonic features of ~100nm.

Since the microtube filling with was not uniform, the transmission varies from theoretical predictions considering fully filled pores. A similar effect was observed by Leonard *et al* for hole-type PhCs around 5μm, where shifts of 70nm in the band edges were observed for liquid crystal infilled PhCs³⁵. Our experiments demonstrate that is possible to shift the PhC features of our microtube-type PhC and exert full control over the shift reversibly and repeatably.

4 Conclusions

Understanding the reaction mechanisms for the VO₂ synthesis allowed us to design a methodology *in situ* filling of PhC structures. The light transmission manipulation in these structures proved to be reversible and repeatable over a broad range of wavelengths in the mid-infrared region of the spectrum. Moreover, the position of the transmission features can be selected by choosing the right geometry and further manipulated due to the phase transition of the filling material. Implications of this achievement are reconfigurable and tunable PhCs for which a plethora of applications can be conceived: optical switches, light circuitry and computing, light guiding and wavelength control for gas sensing. Eventually, following this methodology may lead to program specific spectra by punctually recording defects or geometric patterns in the PhC matrix.

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