Tunable one-dimensional photonic crystals based on metal-organic framework, silica and titania nanoparticles as sensing platforms

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"Smart", stimuli-responsive photonic crystals (PCs) for label-free biological, chemical and physical sensing applications have recently garnered significant attention from various scientific communities, such as photonics, materials chemistry and biotechnology and represent a fast growing research field. Particular interest is attracted by conceptually simple, yet versatile one-dimensional PCs, christened Bragg stacks (BSs), which are interference-based optical multilayer structures consisting of a periodic stack of layers of two different materials featuring high and low refractive indices, respectively. The sensing approach is based on the utilization of such PCs as tunable optical filters capable of dynamically changing their refractive properties when in contact with an analyte of interest, or when exposed to external stimuli such as temperature, electric and magnetic fields, etc. Due to the periodicity of the dielectric lattice of the multilayer structure, which creates a periodic potential for photons in one dimension, the optical spectra of BSs exhibit a forbidden wavelength range for photons with particular energies, called the photonic stop band. The position of the stop band can be modulated by varying the optical thickness (the product of refractive index (RI) and physical thickness) of the layers in response to an external stimulus. In this report we propose photonic crystals designed in particular for vapor and temperature sensing based on the deposition of metal-organic framework/titania and silica/titania multilayers, respectively.

Temperature sensing: SiO_2/TiO_2 photonic crystals

Here we demonstrate a thermally tunable and environmentally responsive optical filter derived from nanoparticle-based TiO_2/SiO_2 one-dimensional photonic crystals.[1] The mechanism of the thermal tunability is based on the thermo-optic effect (TOE), i.e. the dependence of the refractive index on temperature.

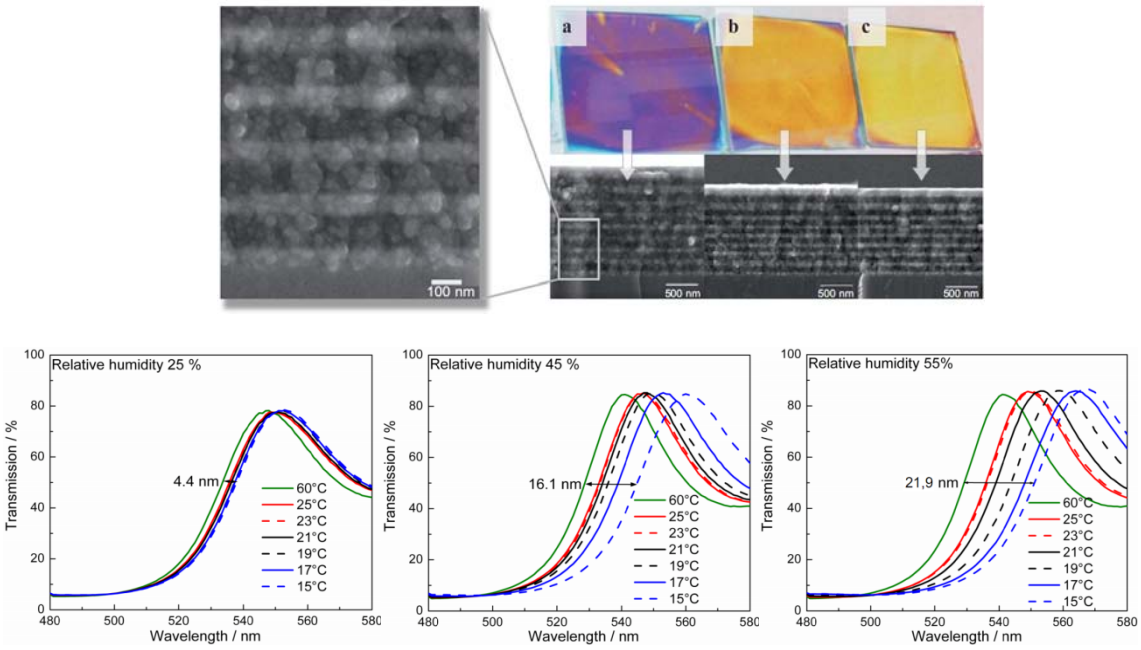

Figure 1: Top image*:* SEM images showing the relationship between the structural color of the TiO_2/SiO_2 Bragg stacks and the thickness of the layers spin-coated at a) 2500, b) 4500, c) 5500 rpm with an acceleration of 1500 rpm s^{-1}. Left: Magnification of the cross-section image 'a' to demonstrate the porous morphology of the layers. The porosity calculated by spectroscopic ellipsometry using the Lorentz-Lorenz equation and toluene as adsorptive is 10 % for TiO_2 and 25% for SiO_2. Bottom image*:* Transmission spectra of the TiO_2/SiO_2 BS shown in Fig. 1(b), demonstrating a blue shift in the temperature range between 15 °C and 60 °C and at various relative humidities (RH): 25%, 45% and 55%. The relative humidity was measured at 20 °C. Spectra between 25 °C and 60 °C are omitted for clarity. The black double arrow indicates the magnitude of the shift *in toto*. Reprinted with permission from [1]. Copyright {2012} American Chemical Society.

The sol-gel method affords a relatively simple, fast and low-cost synthetic pathway to produce SiO_2 and TiO_2 nanoparticles for the assembly of 1D PCs with high optical and structural quality and porous constituent layers. The BSs were obtained by bottom-up assembly based on sequential spin-coating suspensions of nanoparticles on glass substrates. Apart from the high thermo-optic coefficient (TOC) of TiO_2, an additional benefit of SiO_2/TiO_2 PCs stems from their self-cleaning properties provided by the photoactivity of TiO_2 particles under UV irradiation, and their porosity-driven superwetting behaviour. The scanning electron microscopy cross-section images of the BSs are shown in Fig. 1, top image. The layers of TiO_2 and SiO_2 can be identified as bright (higher electron density) and dark stripes, respectively. Varying "structural" colors of the PCs shown arise from variation of the lattice parameters resulting from different spin-coating rotation speeds.
To realize the temperature tuning, the BS, deposited on a transparent glass substrate, was placed on thermoelectric heaters and connected to a resistance thermometer capable of tracking the actual temperature. The BS was positioned between the monochromator and the detector such that the incident beam was normal to the surface of the sample. Notably, the shifts observed were significantly larger than those expected to be induced by the thermo-optic effect alone, with the literature values of TOCs reported for TiO_2 and SiO_2 resulting in shifts of less than 2 nm between 15 °C and 60 °C. In order to explore the nature of the observed enhancement effect, the experiments were performed under ambient conditions (RT, 20 °C) with varying relative humidities (RH) of 25 %, 45 %, or 55 % (Fig.1, bottom image). The inherent porosity of nanoparticle BSs due to interparticle voids provides a quick response pathway to the humidity of ambient air (Fig. 2). Notably, the shift is significantly enhanced with increasing relative humidity of the environment, thereby amplifying the thermal response and thus, sensitivity of the Bragg stack. The magnitude of the spectral shift increases more than fourfold from 4.4 nm to 21.9 nm with a change in relative humidity from 25% to 55% in the temperature range between 15 °C and 60 °C.

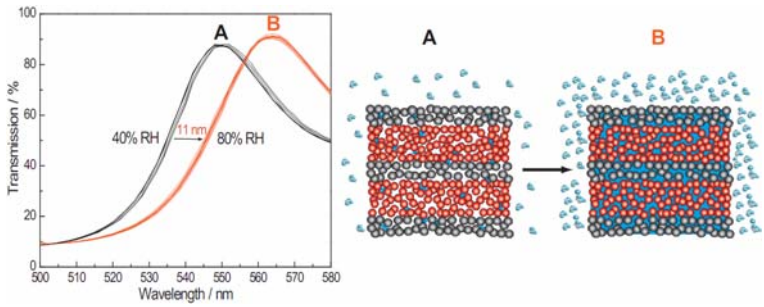

Figure 2: Effect of a change in humidity on the Bragg stack stop band position at constant temperature. Several cycles are shown to demonstrate the reversibility of the water adsorption and desorption. The black arrow indicates 11 nm red shift upon increasing RH from 40% (A) to 80% (B). The scheme on the left demonstrates the increase of the water content in the BS pore network upon augmenting the RH, which results in the enlargement of the effective refractive index of the layers. Reprinted with permission from [1]. Copyright {2012} American Chemical Society.

We assume that at lower temperatures (T < 30 °C) the shifting behaviour is governed by a combination of water adsorption/desorption processes and the thermo-optic effect, whereas at higher temperatures (T > 30 °C) the shift is dominated by the thermo-optic effect and, thus, is essentially linear. Owing to their high inherent porosities and ease of fabrication, nanoparticle-based BSs offer a great potential for the development of sensitive, label-free photonic crystal temperature and humidity sensors.

Vapor sensing: Metal-organic framework photonic crystals

Here we introduce a novel one-dimensional photonic architecture, based on a metal-organic framework (MOF) and TiO_2 nanoparticles, which is used to translate molecular adsorption into an optical response.[2] Additional functionality is imparted to the system by combining textural mesoporosity arising from the nanoparticle based layers with inherent microporosity provided by the MOF material. As a microporous material, the intensively studied zeolitic imidazolate framework ZIF-8 was chosen, which is expected to contribute to enhanced size- and chemoselectivity of the 1D MOF PC.[3]

The preparation of the Bragg stack was pursued by spin-coating alternatingly colloidal suspensions of ZIF-8 and TiO_2 onto silicon substrates. ZIF-8 nanocrystals were synthesized from solutions of $Zn(NO_3)_2 \cdot 6\ H_2O$ and 2-methylimidazole in methanol at high ligand to metal ratio and by separating the particles from the solvent by centrifugation after 30 minutes. TiO_2 nanoparticles were prepared by adding $Ti(OEt)_4$ to aqueous HNO_3 under stirring and heating to 80 °C for 8 hours and subsequent centrifugation. Colloidal suspensions for the spin-coating protocol were obtained by redispersing the particles in defined volumes of DMF, thereby enabling the adjustment of the film thickness by the particle concentration in the suspensions. After each deposition, the films were thermally treated at 200 °C in order to ensure a solvent-free architecture.
The realisation of the multilayered architecture is confirmed by cross-sectional scanning electron microscopy (SEM). In Figure 3 (left) a representative three-bilayer Bragg stack composed of alternating ZIF-8 and TiO_2 layers deposited on a silicon substrate is shown. The X-ray diffraction (XRD) pattern of the ZIF-8/TiO_2 composite likewise confirms the successful integration of ZIF-8 into the 1D PC (Fig. 3, bottom, middle).

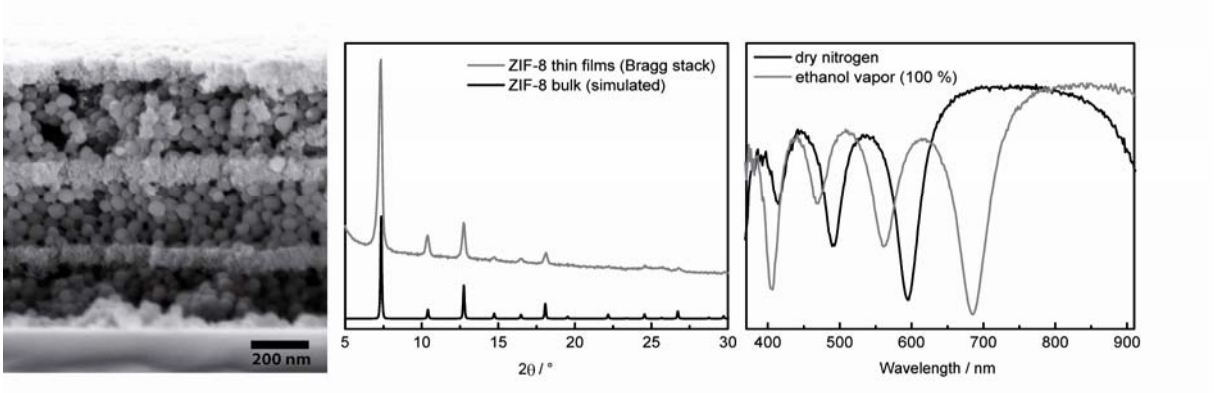

Figure 3: Left: Cross-sectional SEM image of a three-bilayer Bragg stack composed of ZIF-8 layers with an average thickness of 200 nm and titanium dioxide layers with an average thickness of 50 nm. Middle: X-ray powder diffraction patterns of a three-bilayer Bragg stack, revealing the existence of ZIF-8 embedded in the photonic structure, in comparison to simulated data. TiO_2 shows no XRD signature owing to its amorphous nature. Bottom, right: Reflection spectra of a three-bilayer Bragg stack upon exposure to ethanol vapor.

The integration of a microporous MOF material into photonic architectures together with metal oxide layers derived from colloidal solution deposition is supposed to create a unique molecular sieving platform featuring not only size- but also chemoselectivity. The optical response of the MOF Bragg stack to the infiltration of volatile guest molecules was investigated by vapour sorption experiments. According to the optical Bragg equation, the uptake of guest species into the porous layers is supposed to increase the optical thickness of the multilayer and, hence, to induce a color change corresponding to a shift of the optical spectrum. In Figure 3 (right) the reflectance spectra of the Bragg stack are depicted for the analyte-free system and after the adsorption of ethanol vapour at the highest partial pressure ($p/p_0 \sim 1.0$), respectively. The spectral position of the stop band is red-shifted from $\lambda \sim 740$ nm to $\lambda \sim 840$ nm, thus clearly demonstrating the interaction of the analyte with the photonic architecture. The above results indicate the translation of molecular recognition into a readable optical signal without the use of any reporter systems, and hence, label-free optical sensing. We expect that the concept of MOF-based photonic architectures will extend the scope of chemoselective optical transducer systems owing to the great variety and tunability of MOFs or related microporous materials.

References:

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