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1D photonic defect structures based on colloidal porous frameworks: Reverse pore engineering and vapor sorption

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ABSTRACT

Stimuli-responsive 1D photonic crystals, referred to as Bragg stacks, are capable of translating environmental changes into a color read-out through changes in the effective refractive index (RI) of the multilayer system upon infiltration with an analyte. The sensitivity and versatility of prototypic SiO_2/TiO_2 multilayers can be greatly enhanced by the use of nanoparticulate or mesoporous building blocks, or inherently microporous structures such as metal-organic frameworks (MOFs). Here, we introduce a stimuli-responsive ZIF-8 "defect" layer into SiO_2/TiO_2 multilayers in order to combine the high optical quality of a Bragg stack with the characteristic sorption properties of the MOF. The addition of a planar defect layer, either embedded in or deposited on top of the Bragg stack acts as a "dopant" and introduces a narrow band of allowed states in the photonic band gap, which can be utilized for the precise determination of the optical response of the Bragg stack. We demonstrate the impact of layer morphology, layer sequence and the position of the defect on the optical and vapor sorption properties of the photonic architectures. Moreover, a facile process is presented which allows for the clean inversion of the acid-sensitive ZIF-8 defect layer into a mesoporous layer in a one-step fashion, while the layer structure and optical quality of the stack architecture is preserved.

1. Introduction

Periodic multilayer structures built up from dielectric materials with different refractive indices have recently been developed into versatile sensing platforms based on color-tunable, analyte-specific optical readout [1–7]. The capability of these structures, referred to as 1D photonic crystals (PCs) or Bragg stacks (BSs), to translate subtle changes in their chemical environment or internal host–guest interactions into a color read-out has been demonstrated, for instance, by the exposure to gaseous and liquid analytes [4–8]. The presence of guest molecules in the textural pores of the multilayer constituents induces a change in the effective refractive index (RI) and, hence, the structural color of the infiltrated photonic architecture. SiO_2 and TiO_2 layers derived from low-cost sol–gel processing routes are typically used as building blocks in 1D PCs [9,10], as they allow for a high RI contrast and well-defined Bragg reflection peaks with only a few bilayers (BLs) in the stack. A variety of modification schemes have been explored to enhance the response toward environmental changes including the variation of the morphology of the constituting layers such as porosity, size or shape of the building blocks [5,6,11,12]. The sensitivity of sol–gel derived architectures could thus be improved by the use of mesoporous oxides [7,13]. Another possibility is the fabrication of cavity structures whose symmetry is disrupted by a defect layer deposited either inside or on top of a regular BS (referred to as "sandwich" and "top" defect structure, respectively) [6,9,10,14]. The addition of such a layer leads to a narrow band range of allowed frequencies within the photonic stop band, and the well-defined spectral position of the narrow defect mode can be employed as a precise measure for gradually differing analyte concentrations [10]. Finally, the implementation of inherently microporous, chemically functional materials such as metal-organic frameworks (MOFs) may help to

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improve the selectivity of 1D PCs towards molecular-scale analytes. Owing to the modular construction principle of these porous networks built up from metal ions joint by bridging organic linkers, the selectivity and specificity may be greatly enhanced in comparison to conventional metal oxide-based PCs by means of size or shape exclusion and specific host–guest interactions [15,16]. Compared to mesostructured metal oxides, MOFs benefit from well-defined pore systems thus allowing for enhanced analyte specificity as a function of the kinetic diameter of the analyte. Moreover, as a result of the structural variability of MOFs, the affinity toward particular analytes can be fine-tuned from hydrophobic to polar sorptives without the need for additional post-synthetic functionalization steps. The possibility to fabricate MOFs with dimensions reduced down to the nanoscale allows for their integration into thin film devices [17–20], which has recently been demonstrated for ZIF-8 as a component in various multilayer structures [21,22].

In this work, we demonstrate the fabrication of MOF-based defect structures for the first time by depositing ZIF-8 layers on top of regular periodic multilayers, thus breaking their symmetry, as well as by embedding the MOF between two BSs. We show that *via* both approaches clean defect structures are obtained, which are characterized by well-defined Bragg reflection peaks and high reflectivity values. By using different TiO_2 layers derived from either a colloidal dispersion or a sol, we can fine-tune the morphology of the defect architectures which allows for enhanced control of their porosity, while the chemical composition of the PC building blocks remains unchanged. Moreover, we show that the nanoparticulate MOF defect slab can be converted into a mesoporous layer *via* a simple one-step synthesis, alluding to the way in which inverse opal structures are synthesized. The transformation into the reversed pore structure takes place without destroying the original photonic architecture, and the spectral characteristics of the defect structure are preserved, rendering this strategy beneficial for smart defect engineering. Besides the optical quality, we investigated the sensing capability of our samples by exposing them to ethanol vapor at various relative pressures and monitoring *in situ* the spectral shift upon analyte adsorption.

2. Experimental section

2.1. Syntheses

All chemicals used in the syntheses are commercially available and were used without further purification. 2-Methylimidazole ($C_4H_6N_2$, 99%), titanium isopropoxide ($Ti(OiPr)_4$, 97%), 2-propanol (pure) and methanol (puriss) were purchased from Sigma–Aldrich. Tetramethylammonium hydroxide ($N(CH_3)_4OH \cdot 5H_2O$, 99%) and nitric acid (HNO_3, puriss) were purchased from Acros. Ethanol (absolute) was purchased from BfB, hydrochloric acid (HCl, puriss) was purchased from Brenntag, tetraethoxysilane ($Si(OEt)_4$, 99%) was purchased from Merck and zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$, 99%) was purchased from Grüssing.

SiO_2 sol was prepared according to [14]. $Si(OEt)_4$ (1.0 g, 4.8 mmol) and absolute ethanol (8.5 mL) were stirred for 5 min. To this solution, deionized water (0.43 mL) and 0.5 M HCl (0.02 mL) were added consecutively under stirring and the clear mixture was kept stirring at RT until further use. In an alternative route, the SiO_2 sol suspension was obtained by mixing $Si(OEt)_4$, ethanol and 0.1 M HCl (without the addition of water) in volume ratios of 1:10:1 or 2:10:2.

TiO_2 sol was prepared in an analogous fashion to a literature protocol [14]. $Ti(OiPr)_4$ (0.81 g, 2.8 mmol) and 2-propanol (8.3 mL) were stirred for 5 min. To this solution, deionized water (0.026 mL) and 0.1 M HNO_3 (0.02 mL) were added consecutively under stirring and the turbid mixture was kept stirring at RT until further use.

TiO_2 particles were synthesized according to [23]. $Ti(OiPr)_4$ (19.2 g, 65.5 mmol, 20 mL) was added dropwise to deionized water (36 mL) under vigorous stirring. After stirring for 1 h, the resultant white solid was filtered with a 1.2 μm glass microfibers filter (VWR) and washed with deionized water. The solid was mixed with 0.6 M $N(CH_3)_4OH \cdot 5H_2O$ (7.13 g, 39 mmol, 3.9 mL) and transferred to a Teflon autoclave reactor. The mixture was heated at 120 °C for 3 h and subsequently centrifuged at 14,000 rpm for 10 min to remove potential agglomerates from the suspension. The remainder was redispersed in methanol, and before each spin-coating process an appropriate amount of the diluted and sonicated mixture was filtrated with a 0.45 μm syringe filter (VWR) which allowed for enhanced homogeneity of the deposited film.

ZIF-8 nanoparticles were prepared according to a literature synthesis [24]. In a typical experiment, $Zn(NO_3)_2 \cdot 6H_2O$ (0.73 g, 2.44 mmol) was dissolved in methanol (50 mL) and rapidly added to a solution of $C_4H_6N_2$ (1.62 g, 19.6 mmol) in 50 mL methanol. The mixture was stirred constantly throughout the reaction until the solution turned turbid. After 1 h, the nanocrystals were separated from the solvent by centrifugation and washed 3 times with fresh methanol. Stable colloidal suspensions of ZIF-8 were obtained by redispersing the particles after centrifugation in methanol, and repeated sonication.

SiO_2/TiO_2 multilayers were obtained by spin-coating SiO_2 sol and TiO_2 nanoparticles or sol alternatingly on silicon substrates until the desired number of BLs (3–4) was obtained. For depositing the layers within 30–60 s, a rotational speed of 4000 rpm was used at an acceleration speed of 4000 rpm s^{-1} (WS-650SZ-6NPP/LITE, Laurell Technologies Corporation). Different thicknesses of the individual layers were achieved by using either multiple coating steps or by adjusting the material concentration in the respective solvents. After each coating step, the stack was calcined on a hot plate (PZ 28-3TD, Harry Gestigkeit GmbH) at 200 °C for 10–15 min to suppress further thickness changes of the freshly deposited layer. Before the deposition of TiO_2 on top of a SiO_2 layer, the samples were plasma-cleaned for 1 min (Femto plasma-cleaner, Diener Electronic GmbH, air, power: 50%) which significantly improved the adhesion to the SiO_2 surface.

Defect structures were prepared by spin-coating the MOF suspension on a SiO_2/TiO_2 multilayer, using similar spin-coating conditions (4000 rpm at 4000 rpm s^{-1}). The thickness of the MOF layer was adjusted by the number of the deposition steps. After heating at 200 °C for 10–15 min, the stacks were either directly used for characterization and vapor sorption experiments or employed as substrate for sandwich defect structures by coating additional TiO_2/SiO_2 BLs (1–4) on top of the MOF layer. Similarly to the regular SiO_2/TiO_2 BSs, the films were heated after every coating step.

2.2. Characterization

Scanning electron (SE) micrographs and EDX measurements were recorded either with a JEOL JSM-6500F SEM equipped with an Oxford EDX analysis system or with a Merlin (Zeiss) FE-SEM. Additional EDX measurements (for investigating sample **F** where the surface was partially removed by sputtering with Ga ions) were performed with a Crossbeam 1540 EsB workstation (Zeiss). IR spectra were recorded with a JASCO FT/IR-4100 spectrometer. Grazing incidence XRD measurements were conducted with an Empyrean diffractometer (PANanalytical). Ellipsometric measurements were carried out using a Woollam M2000D at angles of 65°, 70° and 75° in the spectral range of 190–1000 nm. The data were fitted between 300 and 1000 nm using a Cauchy-type material as the model layer for MOF thin films, and the respective metal oxide models for SiO_2 and TiO_2 layers. Reflectance spectra for regular BSs and defect structures were simulated using a MATLAB code [25]. In