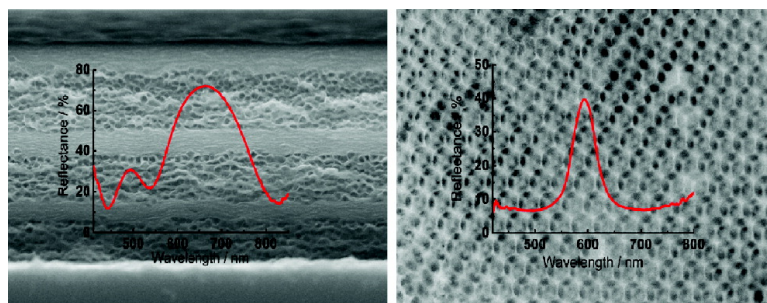


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All-Clay Photonic Crystals

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Functional materials with hierarchical pore size distributions featuring the combined benefits of multiple pore size regimes and a highly “open” morphology have shown potential in a large variety of applications ranging from catalysis to separation and sensing.¹ At the same time, periodic materials structured on the submicron scale are increasingly being targeted for the design of functional photonic devices that make use of tunable structural color emerging from the interaction of periodic nanoscale lattices with visible light.² Recently, we have developed environmentally sensitive 1D photonic crystal (PC) architectures based on the synthetic phyllosilicate Laponite (empirical formula $\text{Na}_{0.7}[(\text{Si}_8\text{Mg}_{5.5}\text{Li}_{0.3})\text{O}_{20}(\text{OH})_4]$), which are capable of translating a chemical response to external stimuli into visibly perceptible color changes.³ As the accessibility of the clay layers is prerequisite for the signal transduction process, an open morphology was ensured by the incorporation of porous titania as high refractive index layers. To further enhance the accessibility, we devised a protocol to fabricate macroporous clay thin films based on a hard templating method using polystyrene (PS) spheres. Full accessibility of these multilayer systems to analytes was confirmed by confocal microscopy on Bragg stacks exposed to Rhodamine 6G solution.^{3b}

In this study, we present “all-clay” 1D and 3D photonic crystals, which combine different hierarchy levels, ordering states and “pore size” regimes with crystallinity, high thermal stability and chemical as well as optical functionality. Whereas hierarchically structured crystalline silicate materials such as clay and zeolite hollow spheres^{4,5} and 3D zeolite or silicate replicas of ordered PS templates⁶ have been fabricated based on bottom-up self-assembly strategies, their utilization as photonic materials remains a major challenge: Their typically large crystal sizes and brittle nature are detrimental to templating and infiltration processes, leading to rapid degradation of the order-induced photonic properties. Moreover, the fabrication of *intrinsically* functional photonic crystals is an emerging subfield in photonic materials research, and we herein present the first examples of chemically responsive PCs entirely based on a layered silicate material.

All-clay 1D periodic structures composed of “dense” and porous Laponite films were obtained by spin-coating stable colloidal suspensions of Laponite nanoplatelets and PS microspheres and removing the sacrificial template postassembly by calcination at 350 °C for 2 h (Figure 1A). Reflectivities of the stop band as high as 70% were achieved owing to high porosities of ~86% of the low-index layers.

Sensing properties of the as-obtained “photonic clays” can be demonstrated by exposing the clay Bragg stack (CBS) to different organic cations in pure ethanol solution; aqueous-based solutions appear to destabilize the clay architecture with exposure time. Figure 1B outlines the response of a three bilayer CBS to 0.03 M solutions of the quaternary tetraethylammonium bromide and surfactant octadecyltrimethylammonium bromide. Red shifts are observed in all cases, and in agreement with previous studies³ the optical response scales with the size of the cations, giving rise to shifts

>80 nm for the larger surfactant. Although the observed size sensitivity is consistent with an intercalation-based analyte uptake mechanism, it is likely dominated by a complex interplay of ion exchange, cointercalation, and analyte adsorption.^{3,7}

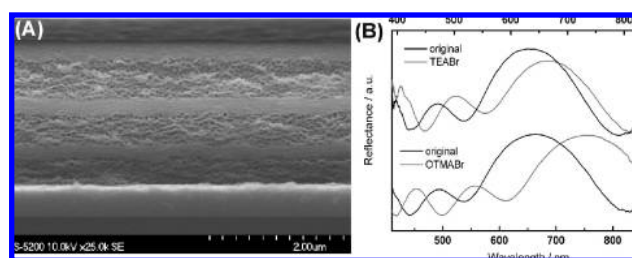


Figure 1. (A) Three bilayer all-Laponite Bragg stack using 100 nm PS spheres as templates in the porous layers; (B) UV–vis reflection spectra of an all-clay Bragg stack (thickness of each layer \approx 125 nm) before and after exposure to solutions of tetraethylammonium bromide (top) and octadecyltrimethylammonium chloride (bottom).

Extending this concept to inverse 3D photonic crystals requires suitable templating or infiltration protocols starting from ordered arrays of monodisperse polymer spheres.⁸ Different infiltration routes were tested for both PS “opal powder”, obtained by sedimentation/centrifugation, and highly ordered PS opal thin films consisting of ~10–20 layers of PS spheres. Whereas infiltration of opal powder featuring template sizes smaller than 235 nm is feasible by vacuum assisted infiltration (Figure 2A and B), the infiltration of as-made PS opal thin films with aqueous suspensions of Laponite by capillary action typically suffered from incomplete infiltration, leading to the deposition of an overlayer and pore clogging (Figure 2C).

As an alternative approach, we employed vertical evaporation-assisted codeposition of stable aqueous suspensions of monodisperse PS spheres (0.4–1 vol%) and Laponite RDS (0.3–1 wt%) on glass substrates (Figure 2D). The assembly is sedimentation-driven, and the ordering process benefits from electrostatic repulsion between PS spheres with negative surface charge and the negatively charged clay nanoplatelets. The evaporation-assisted assembly process occurring at the meniscus of the liquid–air interface facilitates the deposition of ordered Laponite-PS arrays, giving rise to iridescent Laponite-PS hybrid opal films. The choice of negatively rather than positively charged PS spheres is crucial to obtain well-ordered films, as is the use of a temporary sol forming clay such as Laponite RDS (pyrophosphate-stabilized).

Template removal by calcination at 450 °C for 2 h or plasma treatment affords purely inorganic inverted Laponite replicas of the PS template. The as-obtained structures exhibit high thermal stability (>500 °C) and a large tolerance with respect to the size of the sacrificial templates used in the synthesis process (Figures 3, S3, and S4). Using the above methodology, we are able to produce bulk quantities of macroporous Laponite powder (see Adsorption Isotherm in Figure S5) with pore sizes between 50 and 900 nm

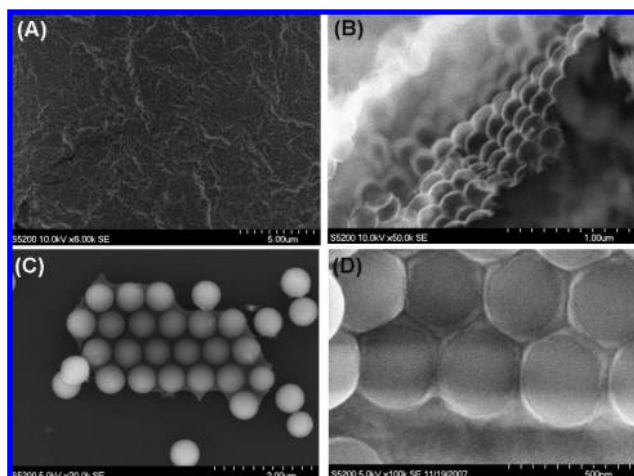


Figure 2. (A and B) Macroporous Laponite “powder” obtained by vacuum infiltration and calcination of 235 nm spheres; (C) infiltration of a 600 nm PS opal film with Laponite and (D) vertical codeposition of 365 nm PS spheres and Laponite.

and a BET surface area of $\sim 320 \text{ m}^2 \text{ g}^{-1}$ by a simple centrifugation–calcination procedure.

Powder XRD measurements (Figure 3C) indicate that the templating and template removal process leave the layered structure of Laponite intact, and no profound change in the peak asymmetries and widths can be observed, pointing at negligible changes in the stacking disorder and crystallite sizes.

Although the high degree of order imparted to the Laponite-PS opal films during the coassembly process somewhat decreases during the replication process, we were able to obtain inverse Laponite opal thin films with satisfactory optical quality at the thinnest film regions. However, the stop band reflectivities are significantly reduced at the bottom part of the film, corresponding to a decrease in film quality as the suspension becomes more concentrated and less stable. As demonstrated by the reflection spectra of inverse Laponite opals (Figure 3D) and even Laponite-PS opals (Figure S6) deposited on glass slides, the dielectric contrast yields satisfactory diffraction efficiencies with the stop bands reaching reflectivities up to 50%. The “infiltration” process translates into a red shift of the stop band (Figure S6), whereas the inversion process leads to a contraction of the photonic lattice corresponding to a blue shift of the stop band.

In this study we have outlined simple bottom-up self-assembly strategies for the synthesis of all-clay 1D and 3D PCs, which owing to their intercalation and ion-exchange capability combined with their low cost and low toxicity may be promising candidates for chemo-optical sensing platforms. The simple large-scale fabrication of porous photonic clay films and powders bodes well for their use as functional hierarchical materials in catalysis, adsorption, and separation science.

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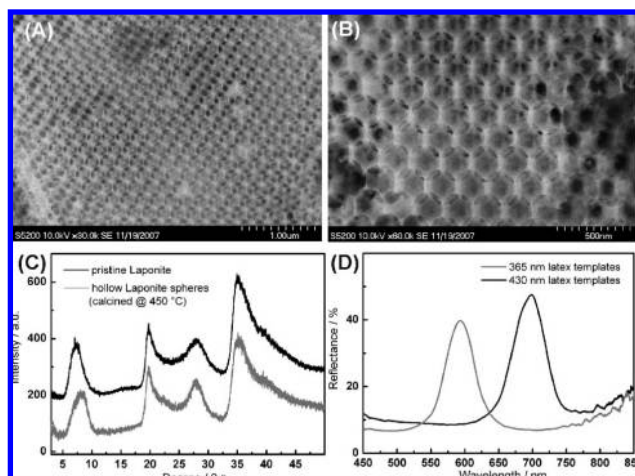


Figure 3. (A and B) 222 nm spheres, calcined at 450 °C; (C) XRD patterns of pristine Laponite (top) and hollow Laponite spheres calcined at 450 °C (bottom); (D) UV–vis spectra of inverse Laponite opals obtained by codeposition and calcination of 365 nm (gray) and 430 nm (black) PS templates.

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Supporting Information Available: SEM images of 1D and 3D Laponite PCs, FTIR spectrum of a CTAB-modified 1D Laponite PC, adsorption isotherm of Laponite hollow spheres and UV–vis spectra of hybrid PS-Laponite 3D PCs. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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