Supplementary Material (ESI) for RSC Advances
This journal is © The Royal Society of Chemistry 2011

Tunable/Switchable One-Dimensional Photonic Crystals Based on a Multilayer Architecture of Layered Double Hydroxides and Titanium Dioxide

Jingbin Han, Yibo Dou, Min Wei,* David G. Evans, and Xue Duan

State Key Laboratory of Chemical Resource Engineering, Beijing University of Chemical Technology, Beijing 100029, P. R. China

*Corresponding author. Tel: +86-10-64412131; Fax: +86-10-64425385.

E-mail address: weimin@mail.buct.edu.cn

Materials

Titanium(IV) ethoxide ($Ti(OEt)_4$, Ti ~20% in ethanol) was purchased from Sigma-Aldrich. $Mg(NO_3)_2 \cdot 6H_2O$, $Al(NO_3)_3 \cdot 9H_2O$, HNO_3 and NaOH were obtained from Beijing Chemical Plant Limited and used without further purification.

Synthesis of MgAl-layered double hydroxide (LDH) and TiO_2 nanoparticles

A colloidal LDH suspension was prepared using a method involving separate nucleation and aging steps (SNAS) developed by our group.[1] Typically, 50 ml of solution A ($Mg(NO_3)_2 \cdot 6H_2O$: 0.1 M and $Al(NO_3)_3 \cdot 9H_2O$: 0.05 M) and 50 ml of solution B (NaOH: 0.3 M) were simultaneously added to a colloid mill with rotor speed of 3000 rpm and mixed for 2 min. The resulting

This journal is © The Royal Society of Chemistry 2012

suspension was removed from the colloid mill and aged at 110 °C for 12 h. The colloidal LDH suspension was obtained by thoroughly washing three times with H_2O and then dispersed in 100 ml of H_2O for spin-coating. Titania nanoparticles were synthesized by dropwise addition of $Ti(OEt)_4$ (6.25 mL) to a stirred solution of 0.1 M HNO_3 (37.5 mL) at room temperature followed by heating the mixture at 80 °C for 8 h. The resulting colloidal suspension was washed three times with H_2O and then dispersed in 50 ml of H_2O for casting.

Fabrication of the LDH/TiO_2 1DPC

To increase the surface wettability of silicon wafers, the wafers were pre-cleaned with Piranha solution for at least 30 min prior to spin-coating. Thin LDH, TiO_2 and LDH/TiO_2 multilayer films were obtained by multiple spin-coating of the aged sols on the treated Si wafers. The first layer in the LDH/TiO_2 film was LDH. Multilayer architectures were fabricated by repeating a multistep procedure involving spin-coating and film aging. After each casting of a LDH or TiO_2 layer at 2000 rmp for 30 s, the aging process was carried out at 150 °C for 3 h in order to increase the cross-linking of the inorganic framework and enhance the adhesive capacity between different layers.

Modulation of optical properties by calcination–rehydration treatment

The Si wafer coated with a LDH/TiO_2 film was annealed at 450 °C for 1 h to produce the MMO/TiO_2 film with a nanoporous structure. For the reverse process, the nanoporous MMO/TiO_2 film was immersed into hot water (100 °C) for 30 min to recover the LDH/TiO_2 structure based on the "memory effect" of LDH materials. The calcination–rehydration treatment was repeated over a number of cycles.

Characterization techniques

This journal is © The Royal Society of Chemistry 2012

Powder X-ray diffraction (XRD) patterns of the samples were collected using a Shimadzu XRD-6000 diffractometer under the following conditions: 40 kV, 30 mA, graphite filtered Cu Kα radiation (λ = 0.1542 nm). Scanning electron microscopy (SEM) images were obtained on a Zeiss Supra 55 field emission scanning electron microscope. Atomic force microscopy (AFM) images were collected using a NanoScope IIIa AFM from Veeco Instruments in the tapping-mode in air. TEM images were obtained on JEOL 2010 microscope operating at 200 kV. The measurement of reflectance spectra of the 1DPCs was conducted using a dual-channel spectrometer (Beijing Purkinje General, TU-1901). The determination of layer thickness, refractive index and porosity of the films was carried out using a spectroscopic ellipsometer (Angstrom Advanced Inc. PHE-102) at an angle of 70° within the spectral range of 300–800 nm. The modeling and fitting of the ellipsometric spectra were performed using the software provided by the manufacturer. The data obtained were fitted to a Cauchy model, which assumes that the real part of the refractive index (n) can be described by:

$$n(\lambda) = \mathrm{A} + \frac{\mathrm{B}}{\lambda^2} + \frac{\mathrm{C}}{\lambda^4} \qquad (1)$$

where A, B and C are constants and λ is the wavelength. The values of the refractive index reported in this study were determined at 633 nm. The porosity changes in the LDH and TiO_2 slabs during the calcination–rehydration process were determined using a reported method based on ellipsometry.[2] In brief, the refractive indices of the film were measured in air and in water using the ellipsometer. The porosity of the film was then calculated by the following equation:

$$p = \frac{n_2 - n_1}{n_w - n_a} = \frac{n_2 - n_1}{0.33} \qquad (2)$$

where p is the porosity of the porous thin film; n_a and n_w represent the refractive indices of air and water, respectively; n_1 and n_2 are the experimentally determined effective refractive indices of the film in air and in water, respectively.

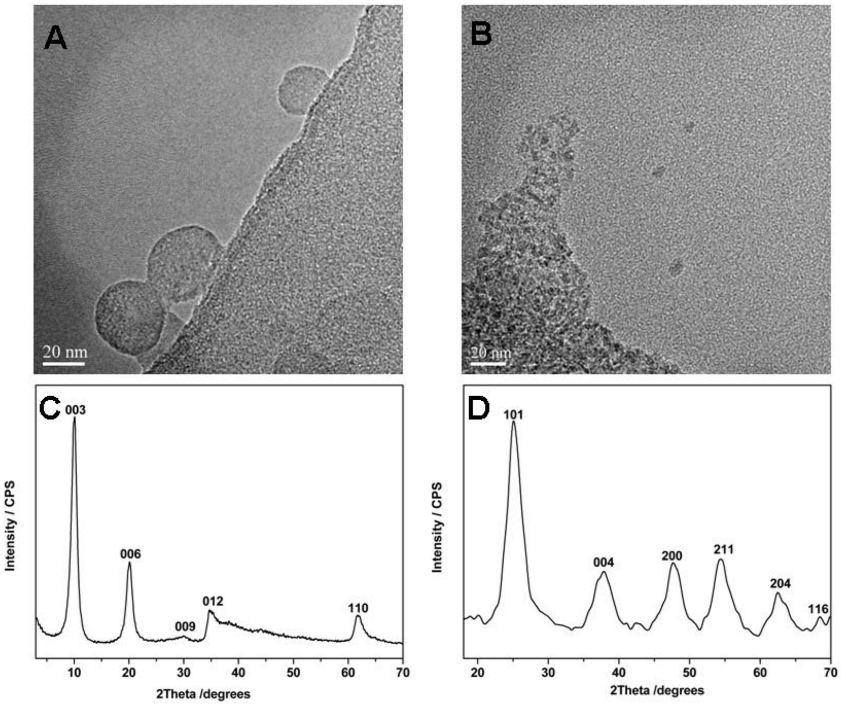

Figure S1. High-resolution TEM images of (A) LDH nanoparticles and (B) TiO_2 nanoparticles; XRD patterns of (C) LDH nanoparticles and (D) TiO_2 nanoparticles.

TiO_2 or LDH films were deposited by the intermittent spin-coating technique. Figure S2 shows the relationship between film thickness and number of spin-coating applications. In both cases, the film thickness displayed a linear growth as a function of spin-coating number, with a correlation of $y_1 = 36.6\, x_1$ (for the TiO_2 stack) and $y_2 = 21.8\, x_2$ (for the LDH stack), in which y denotes the film thickness and x represents the number of spin-coating applications. The average increment in thickness after each spin-coating process was therefore 37 and 22 nm for the TiO_2 and LDH films, respectively. The linear increase in thickness of the TiO_2 and LDH films provides a convenient way to precisely regulate the film thickness by simply varying the coating parameter.

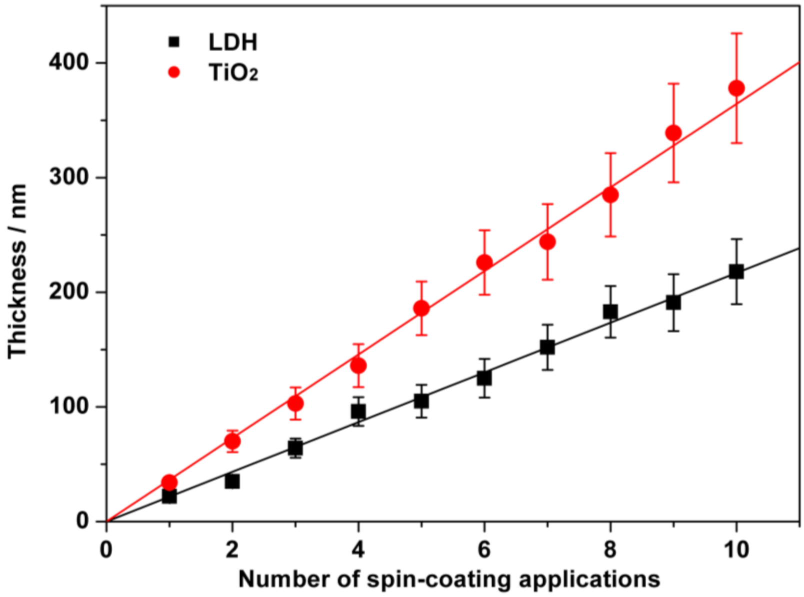

Figure S2. Dependence of the thickness of LDH and TiO_2 films on the number of spin-coating applications.

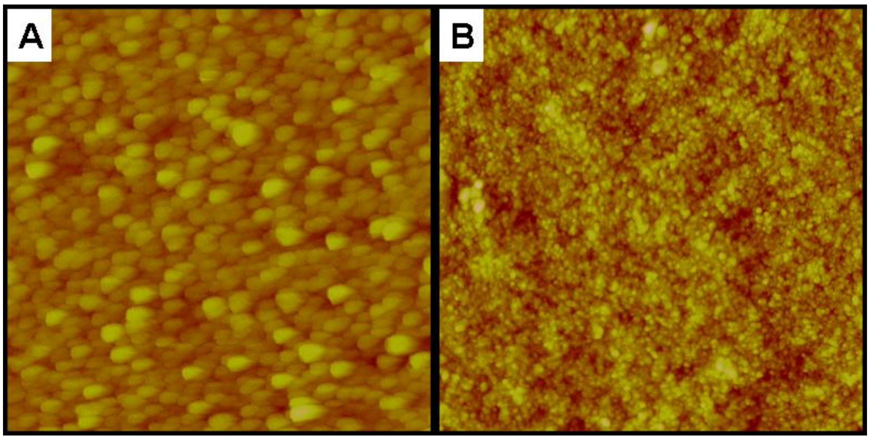

Figure S3. Tapping-mode AFM images of the LDH/TiO_2 films with (A) LDH (N = 5) and (B) TiO_2 (N = 6) as the terminating layer. N denotes the number of slabs in the stack (the scanning size was 1 μm × 1 μm).

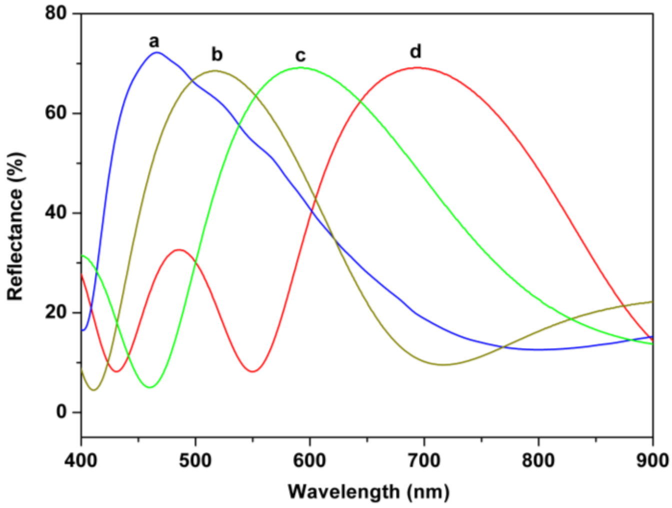

Figure S4. Changes in the reflectance spectra of the LDH/TiO_2 (N = 6) 1DPCs with increasing thickness of the TiO_2 slabs (from a to d).

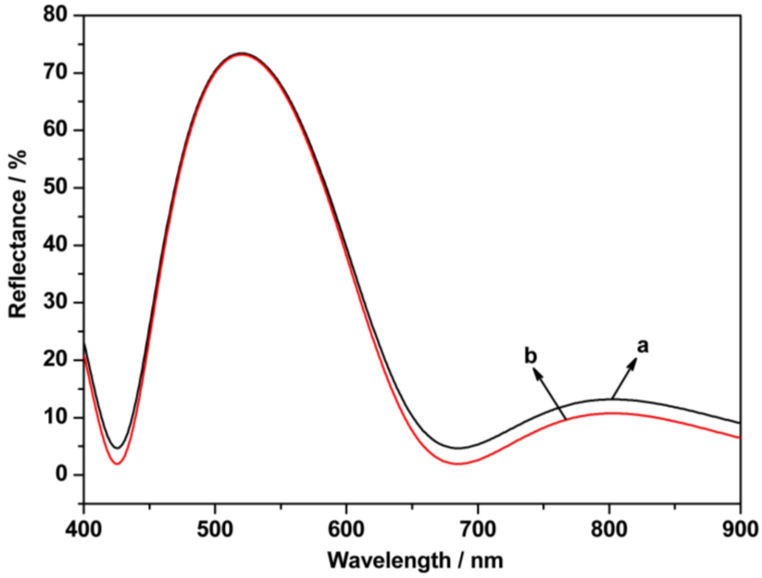

Figure S5. Reflectance spectra of the LDH/TiO_2 multilayer film (N = 6) (a) before and (b) after sonication for 1 h.

This journal is © The Royal Society of Chemistry 2012

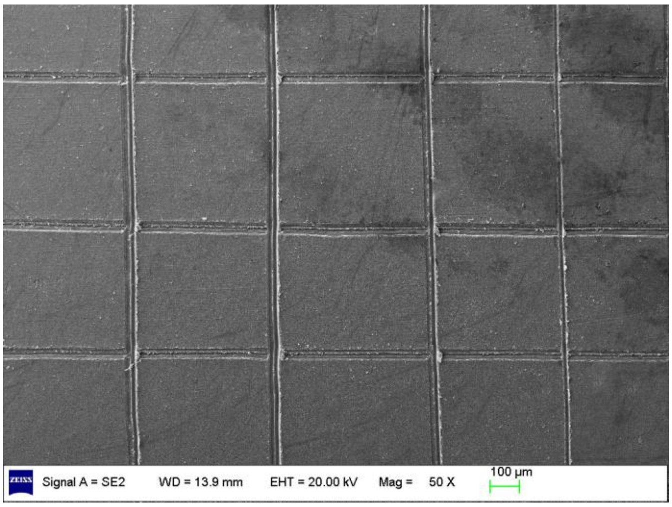

Figure S6. SEM image of the LDH/TiO_2 1DPC tested for adhesion of the film to the substrate.

Reference

[1] Y. Zhao, F. Li, R. Zhang, D. G. Evans and X. Duan, *Chem. Mater*. 2002, **14**, 4286.

[2] D. Lee, M. Rubner and R. E. Cohen, *Nano Lett*. 2006, **10**, 2305.