## PAPER

# Electric field induced structural color changes of SiO$_2$@TiO$_2$ core–shell colloidal suspensions

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A shell size adjustable core–shell nano building block of SiO$_2$@TiO$_2$ using high refractive index materials of TiO$_2$ as shell to coat SiO$_2$ colloidal NPs by one step approach was prepared. Corresponding colloidal suspension of SiO$_2$@TiO$_2$ photonic crystals in propylene carbonate showed a highly adjustable structure color change with the high-refractive index upon applying of electric fields.

## 1 Introduction

In recent years, a particular interest in creatures, plants and even minerals such as Morpho butterflies, *Selaginella uncinata* and opals that can produce a beautiful color without the use of dyes and pigments has drawn great attention from an increasing number of researchers.[1] Named as the structural color, it results from the interference of light from micro- and nano-structures bearing different refractive index materials that are comparable to the visible wavelength of light.[2] Due to bleach free and energy-lost free, these structurally colored materials or photonic crystals are ideal candidates for energy-saving reflective displays and sensors.[3] The color can be tuned by modulating the periodicity or refractive index of materials. By altering the periodicity of the photonic crystals through external stimuli such as electrical, chemical, thermal or mechanical means, an induced swelling or contraction of the photonic crystals coated substrate will result in a shift in the reflected wavelengths of light and thus in a change of color. Among these stimuli, magnetic and electric fields are considered the optimal strategy for modulation of the lattice constants of colloidal crystals for practical applications.[4] However, the magnetic field is inconvenient sometimes once it is applied within a small space, resulting in interference of the fields with each other. This kind of disadvantage of the magnetic field can be avoided through use of electric field as the external stimulus source. For example, various colloidal particles such as silicon dioxide (SiO$_2$),[5] polystyrene,[6] Fe$_3$O$_4$@SiO$_2$ (ref. 7 and 8) *etc.* have been used for the fabrication of photonic crystals with tuning the structural colors under the stimulus of electric field. In order to provide a higher index contrast for increasing the total amount of reflected light, great attention has been focused recently on high refractive index materials. There are a few

investigations reported about high quality crystalline colloidal arrays using high refractive index materials, such as nano-particles (NPs) of TiO$_2$,[10] ZnS.[9] Nevertheless, the use of these spheres is significantly limited to the formation of close-packed photonic crystal systems due to their irregular shape, which results in nonadjustable structural color changes upon triggering of an electric field.[11] Shim *et al.*[12] showed that highly charged TiO$_2$ NPs only exhibited a short range interaction with a maintained position of reflection peak maximum during an applied electric field and suggested weak repulsive forces between NPs. Han and coworkers[13] reported a core–shell building block of SiO$_2$ coated ZnS (ZnS@SiO$_2$) could form a crystalline colloidal array exhibiting good photonic properties under an electric field. Thus, an effective and easy method for high refractive index materials with adjustable color change upon triggering an external electric field is highly desirable.

In this work, we explored a new core–shell nano building block of SiO$_2$@TiO$_2$ using high refractive index materials of TiO$_2$ as a shell to coat SiO$_2$ colloidal NPs by a one step approach. As well known colloidal NPs, the size and shape of SiO$_2$ are easily controlled which resulted in significant adjustment of the particle size and thickness of TiO$_2$ shells. Through the self-assembly of SiO$_2$@TiO$_2$ core–shell NPs through an applied electric field, a colloidal suspension of close packed photonic crystals is formed in propylene carbonate. The reflectance spectrum of the SiO$_2$@TiO$_2$ suspension was investigated under a series of various electric fields. Our results showed that the reasonably adjustable structure color change of high-refractive index materials of SiO$_2$@TiO$_2$ suspension could be achieved not only by controlling the TiO$_2$ shell thickness but also by a change of the applied electric fields.

## 2 Experimental

### 2.1 Chemicals

Tetraethoxysilane (TEOS, AR), titaniumtetraisopropanolate (TTIP, AR), ethanol (AR), NH$_3$·H$_2$O (25%, AR) were purchased

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from Sinopharm Chemical Reagent Company (Shanghai, China). Propylene carbonate (99%) and ethylene glycol were purchased from Aladdin Chemicals (Shanghai, China). Indium tin oxide (ITO) coated glasses with a resistivity of 7 Ω cm were purchased from Corning Corp. All chemicals were used as received without further purification. The water used in this work was deionized (DI) water from a Millipor-Q purification system (Millipore, USA) with resistivity 18.2 MΩ cm.

## 2.2 Synthesis procedures

The synthesis route of SiO$_2$ is based on the hydrolysis of TEOS in an alcohol–ammonia solution, which is similar to the typical ammonia-catalyzed Stöber method.[14] Without separation of SiO$_2$ NPs from the reaction solution, a given amount of TTIP solution was added to the above solution (pH = 11) at 50 °C directly by a peristaltic pump followed by stirring for 4 h. A TiO$_2$ shell on the SiO$_2$ core is thus formed by hydrolysis of TTIP under alkaline conditions.

## 2.3 Preparation of the devices

The photonic display cell consisting of transparent top and bottom electrodes is separated by 200 μm thick epoxy spacers. SiO$_2$@TiO$_2$ suspension (5.4 vol% in propylene carbonate) was injected into the cell using a conventional injection syringe.

## 2.4 Characterization

The morphology and size of the SiO$_2$@TiO$_2$ NPs were examined using FEI Tecnai G2 F20 transmission electron microscopy (TEM). The zeta potential was measured using a particle size analyzer (Malvern, Zetasizer nano zs). The reflection spectra of these SiO$_2$@TiO$_2$ colloidal suspensions under triggering an electric field were measured on an Ocean Optics HR 2000CG-UV-NIR spectrometer coupled with a six-around-one reflection/back scattering probe. The change of SiO$_2$@TiO$_2$ core–shell colloidal suspensions under a series of various electric fields was measured on a semiconductor inspection microscope (LEICA DM2500, Germany). The electric field applied to SiO$_2$@TiO$_2$ core–shell colloidal suspensions was adjusted using a function generator (Agilent, 33220A) for DC power supply.

# 3 Results and discussion

Instead of centrifuging the SiO$_2$ from the alcohol–ammonia solution during the preparation process, the TTIP solution was directly added into the SiO$_2$ solution. Our strategy not only simplified the typical Stöber method but also thus maintained the good dispersibility of SiO$_2$@TiO$_2$ core–shell NPs. Through adjusting the amount of TTIP, SiO$_2$@TiO$_2$ core–shell, NPs with different thicknesses of TiO$_2$ shell are achieved. It was confirmed by TEM images and shown in Fig. 1, that the original SiO$_2$ core with a diameter about 90 nm started to form, and a controlled thicknesses of the TiO$_2$ shell at about 7, 14, 20 and 25 nm are obtained easily.

The structure information of SiO$_2$ NPs and SiO$_2$@TiO$_2$ core–shell NPs is confirmed further by XRD (Fig. 2). An intense broad peak at 22° is attributable to the amorphous silica core (real
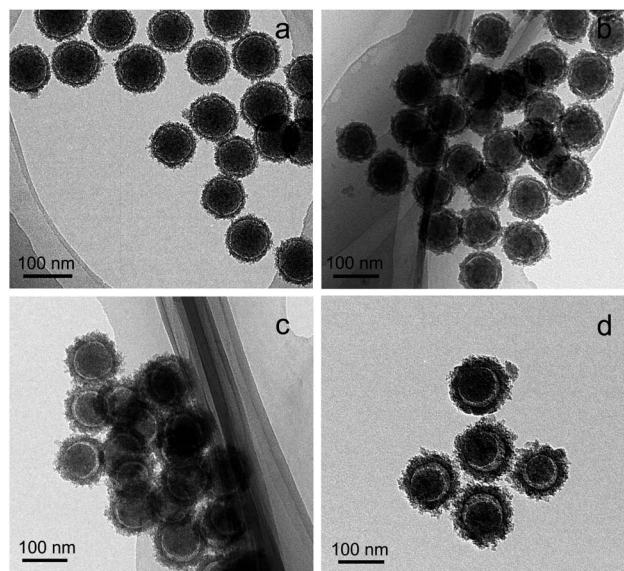


Fig. 1 TEM images with an adjustable TiO$_2$ shell thickness ((a) 7 nm, (b) 14 nm, (c) 20 nm, (d) 25 nm) coating on the surface SiO$_2$ core.

black line).[15] The diffraction spectrum of SiO$_2$@TiO$_2$ core–shell particles shows that the structure of TiO$_2$ shell is amorphous. Interestingly, the size of the SiO$_2$ core constant shrinks with the growth of the amount of TTIP. This may be because the hydrolysis reaction of TTIP is much greater than TEOS, so the H$_2$O in the precursor of initial SiO$_2$ obtained through hydrolyzation of TEOS will be taken away by the TTIP, then the SiO$_2$ becomes smaller and smaller along with increasing the TTIP. We will study the phenomenon in detail in a follow-up work.

The reflection wavelength for normal incident light is estimated by Bragg's law:[6]

$$\lambda = 2dn_{\text{eff}} = \left(\frac{\pi}{3\sqrt{2}\varphi}\right)^{\frac{1}{3}}\left(\frac{8}{3}\right)^{\frac{1}{2}}D\left(n_{\text{p}}^{2}\varphi + n_{\text{m}}^{2}(1-\varphi)\right)^{\frac{1}{2}}$$

where $d$ is the lattice spacing, $n_{\text{eff}}$ is the effective refractive index, $D$ is the particle diameter, and $n_{\text{p}}$ and $n_{\text{m}}$ are the refractive indices of the particles and medium, respectively, $\varphi$ is the volume fraction of the negatively charged particles near the
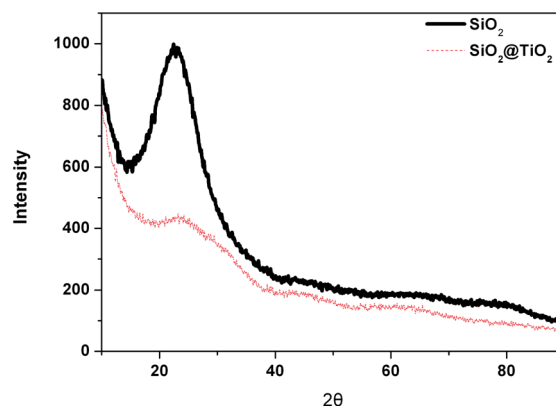


Fig. 2 XRD patterns of SiO$_2$ NPs and SiO$_2$@TiO$_2$ core–shell NPs.

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positively charged electrode. When the electric field was applied to the colloidal suspension, the negatively charged colloidal particles exhibited electrophoretic movement induced by a coulombic force, leading to a variation of $\varphi$ and $\lambda$. As seen from the reflection spectra in Fig. 3a, two reflection peaks at ~425 and ~600 nm of the colloidal suspensions with a $TiO_2$ thickness at 7 nm were recorded in the absence of an electrical potential. Two reflection peaks implied that there are two ordered structures in $SiO_2@TiO_2$ colloidal suspensions. Upon applying an electric field of 1 V, the reflection peak positions were shifted to ~360 nm and ~490 nm, respectively. Increasing the applied positive voltage to 2 V, only one reflection peak at ~360 nm was seen from 300 to 800 nm due to the blue shift and the reflection peak intensity is decreasing. Starting from an applied positive voltage at 3 V, the position of the reflection peak exhibits a red-shift with an increasing peak intensity with the rise of the electric field. Increasing the $TiO_2$ shell thickness, similar phenomena of the reflection peaks starting with a blue shift and ending with a red shift have occurred. The blue and red shifts of the reflection peaks derive from the compression and relaxation of the colloidal lattice. The change in intensity of these reflection peaks originates from the electrophoretic movement and reconstruction of $SiO_2@TiO_2$ colloidal NPs in a cell under an external electric field.

Fig. 4 shows the reflection spectra of $SiO_2@TiO_2$ colloidal NPs suspensions with a shell thickness of $TiO_2$ at 7 nm was recorded at an increasing negative bias voltage. Compared with the reflection spectra of such colloidal NPs suspension under a positive electric field shown in Fig. 3a, the change of reflection peak is similar when the absolute value of the negative bias voltage is less than 2 V. Starting from 3 V, the peak intensity is much lower than the peak intensity shown in Fig. 3a. Due to the
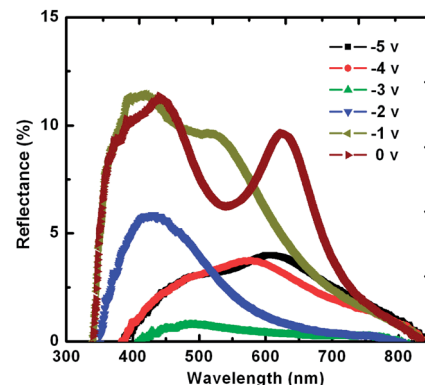


**Fig. 4** Reflection spectra of $SiO_2@TiO_2$ colloidal suspensions with a thickness of $TiO_2$ shell at 7 nm recorded at increasing negative bias voltage. (The time for applying positive bias voltage is 2 min.)

surface, the zeta potential of $SiO_2@TiO_2$ colloidal suspensions in propylene carbonate is about −37.4 mV, the difference thus results from the fact that the reflection spectra are recorded from the positive electrode while the colloidal NPs assemble on the negative electrode when a negative electric field was applied.

The electric field induced structural color changes of $SiO_2@TiO_2$ core–shell colloidal suspensions could be confirmed further *via* the photograph shown in Fig. 5. Upon the field, a positive voltage was applied, and a distinct change of color in the shorter wavelengths could be observed. The lower surface zeta potential of the $SiO_2@TiO_2$ colloidal suspensions leads to a weak repulsive interaction between particles, which resulted in a slight manipulation ability of inter particle spacing. According to a previous report,[16] a larger change of color could be achieved through increasing a higher surface charge of particles.

To clearly show the significant influence in the position of reflection peaks, we investigated the reflection peaks changing of different samples applying a voltage at 2 V. Fig. 6 shows the
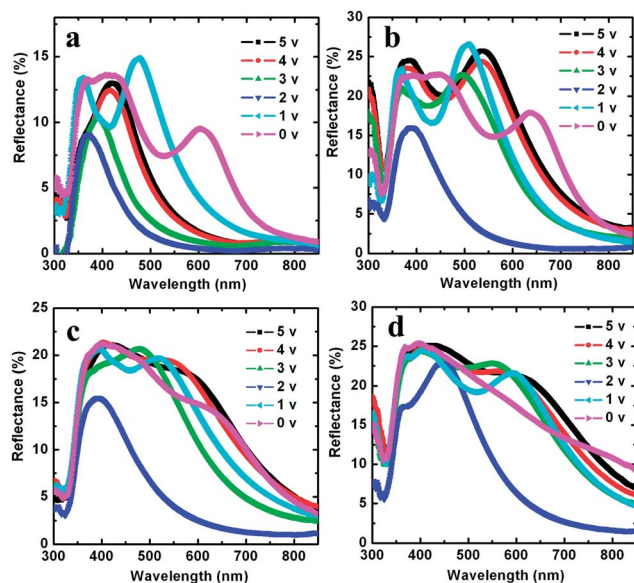


**Fig. 3** Reflection spectra of $SiO_2@TiO_2$ colloidal suspensions with various thicknesses of $TiO_2$ shell recorded at an increasing positive bias voltage. $TiO_2$ shell thickness: (a) 7 nm, (b) 14 nm, (c) 20 nm, (d) 25 nm. (The time for applying positive bias voltage is 2 min.)
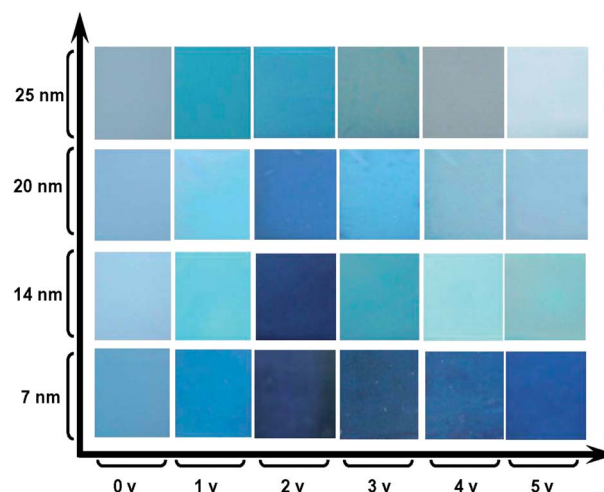


**Fig. 5** Photos of $SiO_2@TiO_2$ colloidal suspensions with different thicknesses of $TiO_2$ shell recorded at increasing positive bias voltage. (Concentration: 5.4 vol% colloids in propylene carbonate, the time for applying a positive bias voltage is 2 min.)

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variations of the peak position as a function of the $TiO_2$ shell thickness. It could be seen that the reflection peaks shift to longer wavelengths when the shell thickness increases, which results from the modulation of the volume ratios between the core and the shell. Since $TiO_2$ has a much higher refractive index than $SiO_2$, the effective refractive index of $SiO_2@TiO_2$ particles thus increases with the increase of the $TiO_2$ shell thickness. According to the theory of Bragg's law[6] ($\lambda = 2dn_{eff}$), the value of $n_{eff}$ increases with the increase of the effective refractive index of $SiO_2@TiO_2$ particles. So, the diffraction wavelength $\lambda$ for normal incident light shifts to longer wavelengths.

To investigate the reversibility of the reflection spectra triggered by an external electric field, we took off the DC power supply at a different electric field. As shown in Fig. 7, the reflectance peak almost returned to its original position after turning off the DC power supply at 1 V after 12 min. With increasing the electric field, the reflectance peak can't return to its original position though extending the time, which resulted from the formation of particle aggregates on the electrodes. This could be proved by observing the aggregation morphology evolution after applying the electric field.

The change of structure will lead to a variation of the reflection spectra, to investigate the relationship between a self-assembled colloidal structure and applied electric fields, three typical samples were prepared through dropping a colloidal solution on the ITO glass in air without voltage, on the electrode surface after applying a negative or positive voltage in the test cell. It was shown in Fig. 8 that homogeneous multilayers $SiO_2@TiO_2$ core–shell NPs were formed on the surface without or with a negative voltage. Once a positive voltage being applied, a raised structure was formed.

The change of structure is attributable to the electrophoretic movement of colloidal particles under a DC field.[17] This could be observed further through a metallographic microscope. Fig. 9 shows the structure evolution under a positive electric field with increasing the field strengths. Without an electric field applied, the negatively charged particles are well dispersed because of the electrostatic repulsion (Fig. 9a). Once a 1 V
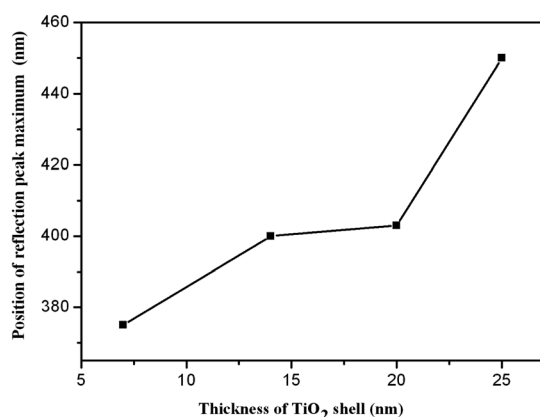


Fig. 7 Time-dependent reflection spectra of $SiO_2@TiO_2$ colloidal suspensions with the $TiO_2$ shell thickness of 7 nm after turning off the DC power supply at different electric fields. (a) 1 V, (b) 1.5 V, (c) 3 V, (d) 5 V.

electric field is vertically applied, the electrostatic attraction between negatively charged particles and a positively charged electrode will result in electrophoretic movement. The negatively charged particles will move to the positively charged electrode on the vertical dimension. The global motion of particles would lead to a flow of the medium and more and more negatively charged particles would be seen on the positively charged electrode. The boundary lines are the collection
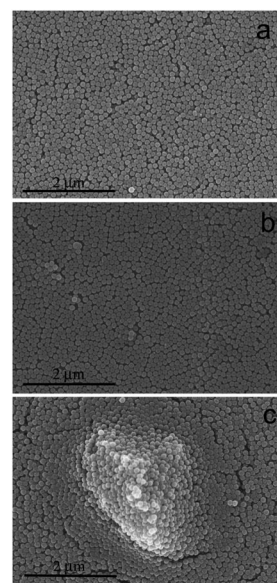


Fig. 8 (a) SEM images of the colloidal solution dropping on the glass in the air; (b) SEM images of the colloidal layers formed on the negative electrode surface in the test cell after applying voltage; (c) SEM images of the colloidal layers formed on the positive electrode surface in the test cell after applying voltage.



Fig. 6 Change of the reflection peak position of $SiO_2@TiO_2$ colloidal suspensions under a fixed external positive electric field at 2 V.

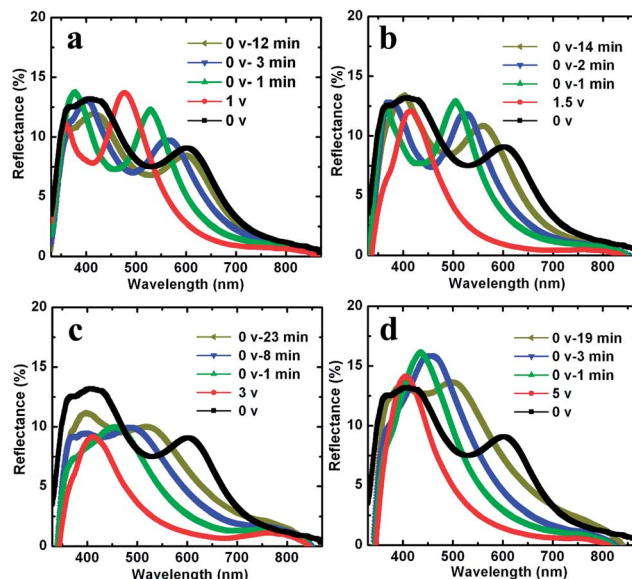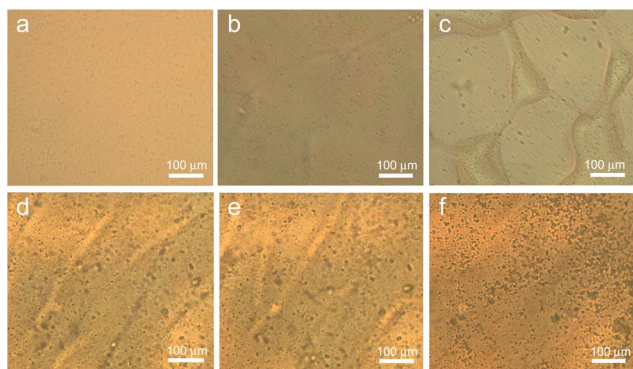This journal is © The Royal Society of Chemistry 2014

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**Fig. 9** Photomicrograph of $SiO_2$@$TiO_2$ colloidal suspensions with a $TiO_2$ shell thickness of 7 nm at different applied electric fields. (a) 0 V, (b) 1 V, (c) 2 V, (d) 3 V, (e) 4 V and (f) 5 V.

of the particles (Fig. 9b). The boundary lines expand into bumps because of the more rapid flow of the medium and more particles when a 2 V electric field is applied (Fig. 9c). All of the particles are similarly charged and have a diffuse ion cloud polarized by the electric field. Accordingly, the electrostatic repulsion is present as particles approach each other, so the bump will disappear due to the repulsion between particles when the voltage is increased to 3 V (Fig. 9d). With a sufficiently strong current, the particles move toward one another across the electrode surface. This phenomenon is called lateral attraction[17] which is strong enough to overcome electrostatic repulsion, so these colloidal particles begin to aggregate due to the lateral attraction at 4 V (Fig. 9e). After the electric field reaches 5 V, a mass of aggregations of colloidal particles can be observed.

## 4   Conclusions

In summary, size adjustable core–shell $SiO_2$@$TiO_2$ colloidal nanoparticles are prepared, using high refractive index materials of $TiO_2$ as a shell to coat $SiO_2$ colloidal NPs by a one step approach. The corresponding colloidal suspension of $SiO_2$@$TiO_2$ photonic crystals close packed in propylene carbonate showed a highly adjustable structure color change with a high-refractive index upon the applied electric fields. The increase in the thickness of $TiO_2$ shell can tune the reflection peaks. This suggested that the reflectance spectrum can be tuned by adapting the ratios between the low refractive index core and the high refractive index shell. The $SiO_2$@$TiO_2$ photonic crystals have potential applications in a wide range of optical applications, including optical switches and display devices due to reversibility and low actuation voltage.

## Acknowledgements

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