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Generation of Highly Ordered 3D Vivid Monochromatic Coloured Photonic Crystal Films Using Evaporative Induced Technique

Ikhazuagbe H. Ifijen[1*], Esther U. Ikhuoria[2*]
[1]*Department of Research Operation, Rubber Research Institute of Nigeria, P.M.B. 1049, Benin-City, Nigeria*
[2]*Department of Chemistry, University of Benin, P.M.B. 1154, Benin City, Nigeria*
**Corresponding authors; e-mail: larylans4u@yahoo.com (Ifijen), esther.ikhuoria@uniben.edu (Ikhuoria)*

Abstract

Structural coloured crystal films have attracted immense attention because of numerous applications like optical sensing, anti-counterfeiting and photonic fabrics. Herein, we successfully generated highly periodic three-dimensional (3D) monochromatic structural crystal films with brown, turquoise, blue and yellow colourations from as-synthesized poly(styrene-methyl methacrylate-acrylic acid) or P(St-MMA-AA) colloidal latex via the evaporative induced self-assembly technique. The colours were controlled through the modulation of their crystal lattice by varying their microspheres diameter from 180 nm, 120 nm, and 260 nm to 150 nm. Scanning electron microscope and atomic force microscope (SEM/AFM) analyses showed that the photonic crystal particles readily assembled into an impeccable closely-packed three dimensional (3D) ordered hexagonal structure with multiple monolayer arrangements. Transmission electron microscope (TEM) analysis revealed that the synthesized P(St-MMA-AA) colloidal particles have a core-shell morphology. The ability to deliberately fabricate photonic crystals by synthesizing polymer colloidal particles with a specific desired size for the fabrication of monochromatic colours would be very useful in the field of optical sensing.

Keywords: core-shell; crystal films; photonic crystal films; monochromatic

Introduction

Electromagnetic radiation can be diffracted by structural periodic materials provided the wavelength of light corresponds to the lattice constant (Xia et al. 2000). These types of materials are known also known as photonic crystals (PCs). They can be defined as dielectric periodic materials with different refractive indices generated from alternating regions of spatially periodic structures (Jukam and Sherwin 2003). Due to the possibility of modulating the dielectric constants of these materials, the propagation of photons can be tuned in a similar way semi-conductor does for electrons, that is, in the periodic lattice, there is an impermissible gap in the photonic dielectric periodic structure that can prevent the emergence of optical modes. As a consequence, the manipulation, confinement and control of light in three dimensions have been made possible because of this unique property. Previous studies have shown that photonic crystals (PCs) can, totally hinder the transmission of photons regardless of their direction of flow or polarization; localize photons to certain area at specified frequencies; control the dynamics of an impromptu emission activity and serve as a lossless waveguide to control the movement of light along a desired direction (Wang et al. 2011). They can be applied in practical applications such as magnetic displays (Kohoutek et al. 2018), enhanced photovoltaics (Karg et al. 2015, Kohoutek et al. 2018), photonic fabrics (Zhao et al. 2016), anti-

counterfeiting technologies (Parchine et al. 2016) and optical sensing (Cai et al. 2015).

In recent times, interest in photonic crystals (PCs) as a new prospect for colour elements has been shown by several researchers (Segal et al. 2015, Chen et al. 2016). The modulation of refractive index or lattice constant by manipulating properties like mechanical stimuli (Pouya et al. 2016), electrical (Pouya et al. 2016), thermal (Markos 2016) and optical (Gur et al. 2015) properties can be used to control the structural colours of the photonic crystals (PCs). For example, Kim et al. (2018) produced a full-colour reflective-type display with high colour purity, cycling durability and high optical efficiency by modulating the electrical phase retardation via liquid crystal layer (LC). One major challenge in the fabrication of photonic crystals is obtaining structural colours that are monochromatic, that is, crystals that retain their colours regardless of the direction of the viewing angle. Monochromatic nature of PCs is a major requirement for applications that involve sensing. This is because when photonic crystals (PCs) with colour tunable properties are used for sensing application, it may be very difficult to establish whether a colour response, if any, will be due to changes in external stimuli or colour tunable nature of the photonic crystals (PC) (Ifijen et al. 2019b).

This study prepared a series of fascinating highly ordered three-dimensional intense monochromatic photonic crystal colours from poly(styrene–methyl methacrylate-acrylic acid) colloidal microsphere via the simple evaporative induced self-assembly procedure that may have practical applications in optical sensing.

Materials

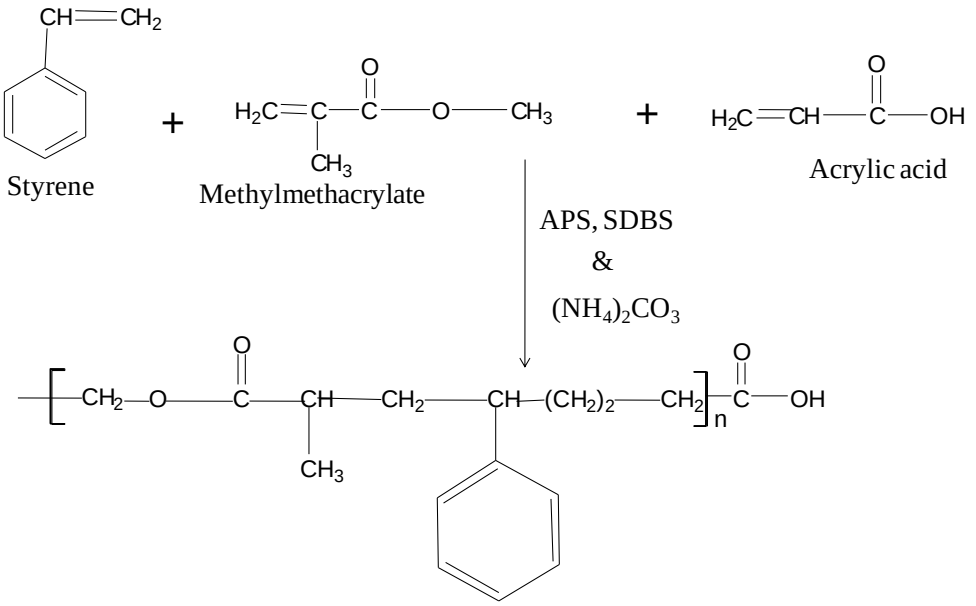
Methyl-methacrylate (MMA), ammonium per-sulfate (APS), ammonium bicarbonate, styrene (St), acrylic acid (AA), sodium hydroxide and sodium dodecylbenzene sulfonate (SDBS) chemicals were obtained from sigma Aldrich inc. (USA) and were of AR grade. The supplied chemicals were used as received.

Synthesis of monodispersed poly(styrene-methyl methacrylate-acrylic acid) latex

Monodispersed P(St-MMA-AA) colloidal microspheres were prepared via batch soap seeded emulsion polymerization technique as described by Wang et al. (2016) with slight modifications. In a routine experimental procedure, acrylic acid (AA) (0.62 g), methyl-methacrylate (MMA) (0.735 g), sodium dodecylbenzene-sulfonate (SDBS) emulsifier (0.0042 g), ammonium carbonate ($(NH_4)_2CO_3$) buffer agent (0.085 g), styrene (3.17 g) and de-ionized water (16.5 g) were transferred into a 50 ml two-neck vessel and then stirred at 410 rpm for 20 minutes at 80 °C in a nitrogen inert environment. Thereafter, 0.08 g of ammonium persulfate (APS) was introduced in the mixture to initiate the polymerization process. The other monodispersed P(St-MMA-AA) samples were similarly prepared by varying their reaction parameters. The proposed/possible reaction scheme for the formation of P(St-MMA-AA) latex is depicted in reaction Scheme 1.

Fabrication of structural coloured colloidal crystal films

Coloured colloidal crystal films were generated as described by a published procedure (Ifijen et al. 2019a). The core-shell P(St-MMA-AA) crystal films were fabricated from the as-synthesized colloidal microspheres via a vertical deposition technique. The colloidal particles were self-assembled after maintaining the assembly system at 55 °C for 24 h in a water bath and then dried with the aid of vacuum oven.



Poly(styrene-methylmethacrylate acrylic acid)

Scheme 1: Reaction stages leading to the formation of P(St-MMA-AA) microspheres.

Characterization techniques

Atomic force microscope in the tapping mode (Bruker Multimode, Germany), high-resolution transmission electron microscopy (TECNAI F2G20 HRTEM) and Olympus BX51 polarized optical microscope and scanning electron microscope (JEOL-JSM 5600LV) were used to examine the morphology of the as-synthesized P(St-MMA-AA) microspheres and the fabricated colloidal crystal films. Dynamic Light Scattering (DLS) (Nano-Zetasizer, Malvern Instruments) was used to determine the average particle size and polydispersity index (PDI) of the P(St-MMA-AA) samples at 25 °C, under the scattering angle of 173° at 6333 nm wavelength. The FTIR spectrophotometer from Perkin Elmer was used to determine the functional groups of the prepared latex samples.

Result and Discussions

Functional groups of the as-prepared P(St-MMA-AA) colloidal microspheres

The FTIR spectrum for determining the functional groups of the prepared P(St-MMA-AA) latex is presented in Figure 1. The broad intense peak at 1202 cm^{-1} can be attributed to the C-O stretching vibration in the ester bond, confirming the formation of the ester group shown in reaction Scheme 1 (Liu et al. 2015). The absorbance peak at 1727 cm^{-1} is due to the existence of C=O (carbonyl functional group of an acid) (Liu et al. 2009, Ifijen et al. 2019a). The broad absorbance peak at 3496 cm^{-1} was attributed to the presence of -OH in the sample which complemented the C=O to indicate a carboxylic acid (–COOH) functional group. The bands at 1490 cm^{-1} and 1454 cm^{-1} are solely due to the stretching vibration in the aromatic C=C-C bond (Ikhuoria et al. 2018, Omorogbe et al. 2019). The second peak for aromatic C=C was observed at 1603 cm^{-1}. The appearance of the peaks at 758 cm^{-1} and 699

cm^{-1} signified the existence of -C-H out-of-plane bending vibrations in aromatic bonds (Kim et al. 2009). The observed functional groups from the as-synthesized latex correspond with the band of FTIR absorbance peaks of P(St-MMA-AA) latex (Ikhuoria et al. 2018, Ifijen et al. 2019a).

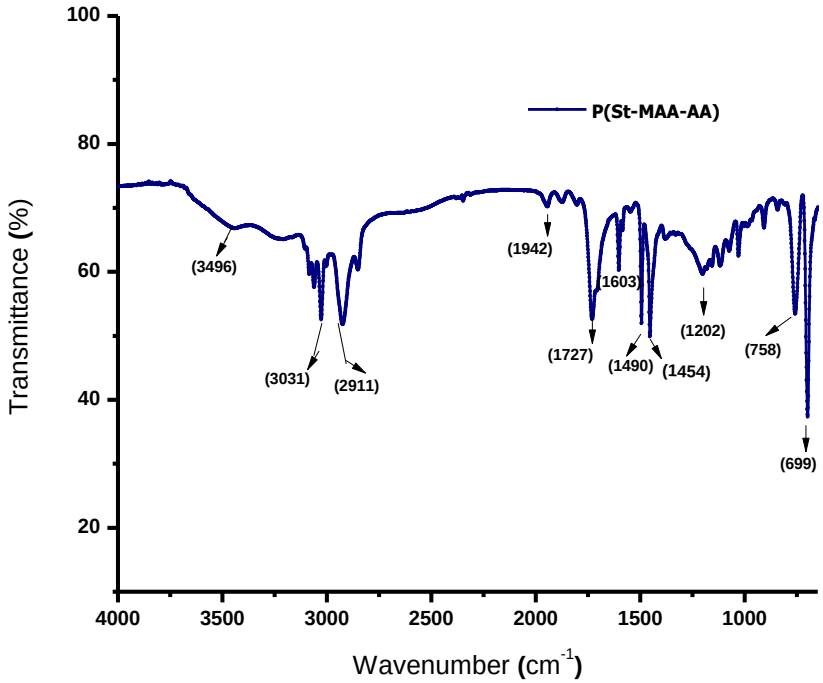


Figure 1: Fourier transform infrared (FTIR) spectrum of the as-synthesized P(St-MMA-AA) latex.

Average particle diameter, polydispersity index and zeta-potential of P(St-MMA-AA) latexes

The average particle sizes of P(St-MMA-AA)$_{1,2,3,4}$ were found to be 220 nm, 150 nm, 305 nm and 168 nm, respectively. The prepared terpolymer particles were seen to be highly monodispersed due to the polydispersity (PDI) index of << 0.1 (Masarudin et al. 2015) for all the prepared samples (Figure 1). The as-synthesized P(St-MMA-AA)$_{1,2,3,4}$ respectively have zeta potentials of –35.72 mV, –32.66 mV, –30.11 mV and –34.90 mV (Table 1). The results show that all the synthesized P(St-MMA-AA) samples have good colloidal stability (Masarudin et al. 2015, Hanaor et al. 2012).

Table 1: Average particle diameter and other properties of P(St-MMA-AA) spheres

	P(St-MMA-AA)$_1$	P(St-MMA-AA)$_2$	P(St-MMA-AA)$_3$	P(St-MMA-AA)$_4$
Average particle diameter (nm)	220	150	305	168
Polydispersity Index (Pdl)	0.068	0.075	0.104	0.038
Zeta-potential (mV)	–35.72	–32.66	–30.11	–34.90

Transmission electron analysis of the as-prepared P(St-MMA-AA) photonic crystal films

Figure 2 depicts the transmission electron micrographs of the prepared P(St-MMA-AA) latex particles. The obtained particles were observed to be spherical in shapes with variable average particle diameters (Figure 2). Two distinct layers, which signified core-shell morphology, were observed for all the examined particles. The dark and light layers represent a polystyrene core and poly(methyl methacrylate)/ poly(acrylic acid) shell. With the aid of image J software, the core/shell average particle diameters of the latex samples (Figure 2(a, b, c and d)) were observed to be 20 nm/180 nm, 10 nm/120 nm, 35 nm/260 nm and 8 nm/150 nm, respectively. The different average particle diameters observed for the synthesized samples were achieved by varying certain reaction parameters such as initiator amount, surfactant amount and temperature of reaction. The obtained sizes were observed to be slightly different from that obtained using the dynamic light scattering analysis (DLS). This may be due to the fact that DLS measures the hydrodynamic diameter of particles.

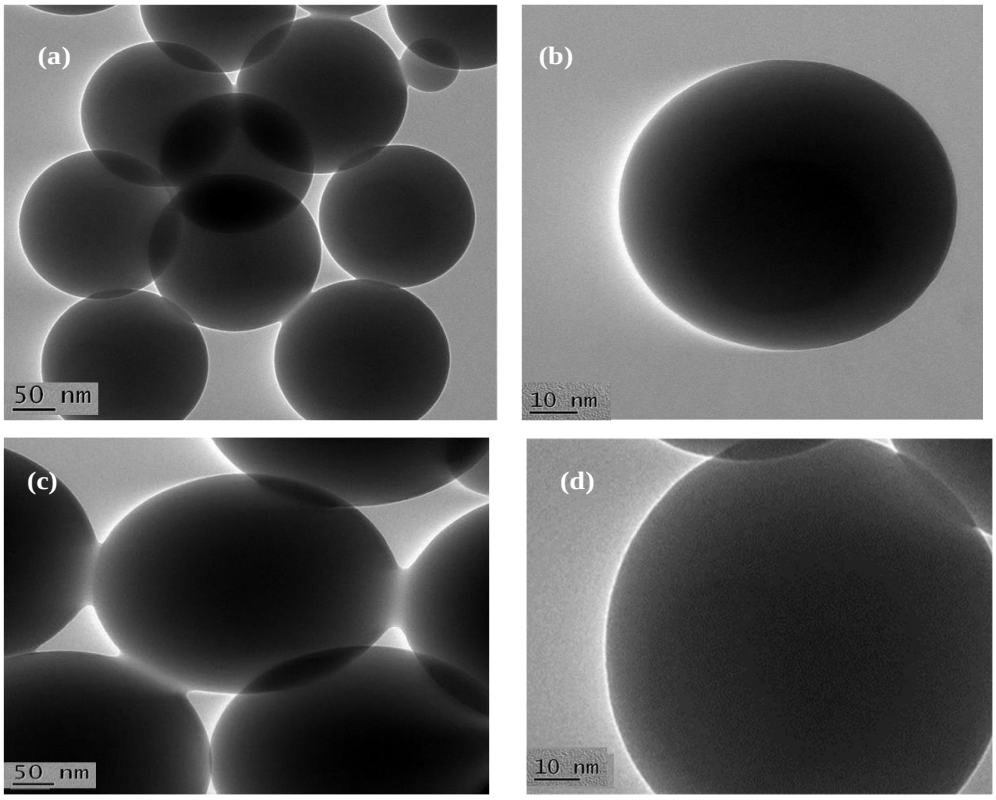


Figure 2: Transmission electron micrographs of (a) 200 nm (b) 130 nm (c) 295 nm (d) 158 nm as-synthesized P(St-MMA-AA) microspheres.

Scanning electron microscopic analysis of the fabricated crystal films

Photonic crystal films were fabricated from the as-synthesized colloidal latexes on glass slides via the evaporative induced self-assembly process at a controlled temperature of 55 °C. Figure 3 (a, b, c and d) shows the scanning electron micrographs of the fabricated coloured films, while the insets

show the coloured photonic crystal films generated on the surface of a glass slides.

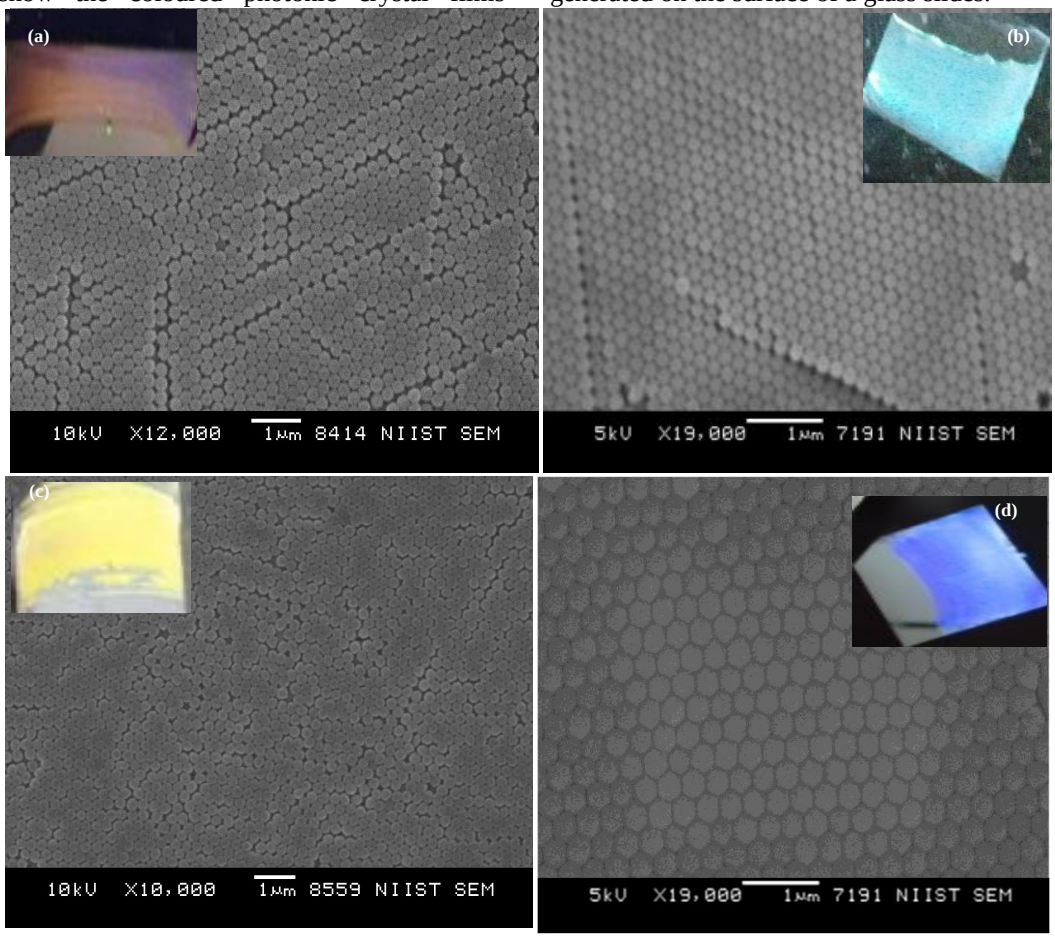


Figure 3 (a, b, c and d): Scanning electron micrographs of the fabricated photonic crystal films with insets of the obtained photonic crystal films on glass slides.

The crystal films were fabricated with average particle diameters of 180 nm, 120 nm, 260 nm and 150 nm P(St-MMA-AA) microspheres. The obtained crystal films respectively displayed brown, turquoise, yellow and blue colourations which did not change colour with variations in observation angles (monochromatic colour). The observed monochromatic structural colours could be due to the difference in the average particle diameters of the as-synthesized P(St-MMA-AA) latexes (Ikhuoria et al. 2018). The results of this study are quite different from the colour tunable nature of the photonic crystal films obtained from our previous study (Ifijen et al. 2019b). Comparing the microscopic results of this study (Figure 2, 3, 4 and 5) to a previous work on poly(styrene-butyl acrylate-acrylic acid) (P(St-BA-AA) latex (Ifijen et al. 2019b); it can be asserted that the photonic nature of the obtained photonic crystals (PCs) is not affected by the nature of terpolymer latex used but can be influenced by the monodispersity of particles, average particle diameters and the nature of particles arrangements. This assertion was made due to the fact that the PCs generated using P(St-MMA-AA) latex were observed to be similar to the poly(styrene-butyl

acrylate-acrylic acid) latex PCs reported by Ifijen et al. (2019b). However, the poly(styrene-methyl methacrylate acrylic acid) particles were also established to be more thermally stable than poly(styrene-butyl acrylate-acrylic acid) particles (Ifijen et al. 2019a). As such, it is therefore recommended to use P(St-MMA-AA) latex rather (P(St-BA-AA) latex for applications that involve a more improved thermal stability.

The monochromatic nature of their colours is of great importance because of their possible applications in optical sensing. Due to the fact that the obtained colours do not change irrespective of their viewing angles, the colloidal microspheres to be used in the photonic crystal film fabrication can, for instance, be incorporated with a molecular recognition agent that responds to a specific external stimulus. When this is the case, a change in colour with respect to a particular external stimulus would without any doubt be attributed to the responsive property confer on the crystal films by the incorporated molecular recognition agent. Whereas, if the colour of the crystal film is tunable even when its microstructure has not been incorporated with a molecular recognition agent, it will be very difficult to determine whether the fabricated photonic crystal films would be responsive to a desired external stimuli after incorporation with a molecular recognition agent because the tunable nature of the film may interfere with the colour change that may have resulted from the responsive nature of the film. The wavelength of the incident light that resulted from diffraction can be estimated by a modified Bragg-Snell equation (Zhao et al. 2012).

Unlike other materials that display colours based on the nature and amount of light absorbed, the beautiful colours demonstrated by these generated P(St-MMA-AA) colloidal crystal films may be attributed to the diffraction and scattering of light. The periodicity and crystal lattice of PCs have been demonstrated by previous studies to be a significant determinant that regulates the colour display characteristics of colloidal crystal films (Zhao et al. 2012, Ikhuoria et al. 2018). SEM analysis revealed that the colloidal latex particles readily assembled into an impeccable closely-packed three dimensional ordered hexagonal structure after the completion of the self-assembly process (Figure 3). The driving force of this process has been shown to be the convective force initiated from the solvent evaporation and forces of capillary existing between the phase interlinking the meniscus and the surface of the glass slide (Dumanli and Savin 2016, Ikhuoria et al. 2018, Ifijen et al. 2019a).

Optical electron microscope analysis of the fabricated P(St-MMA-AA) films

Figure 4 shows the optical microscope images of the generated photonic crystal films with inset of multiple monolayer arrangements revealed by SEM micrographs. The optical microscopic results showed significant cracking with typical interconnected branched patterns. The estimated inter-crack diameters seen on the surfaces of the fabricated photonic crystal films in Figure 4 (a, b, c and d) were 1-2 μm, 4-5 μm, 2-3 μm and 5-6 μm, respectively. Cracks that have parallel straight lines along the surface of the films in the growth direction were seen to be scattered in several areas of the colloidal crystal films. Also, the compact hexagonal structure of the crystal films is retained. The emergence of cracks in some areas of the colloidal crystal structure could be due to evaporation of solvent during the growth stage. The contraction caused by the solvent evaporation process is responsible for the emergence of crack faults (Li and Marlow 2006, Rong et al. 2011). However, the monochromatic nature of the generated crystal films was not hindered by the observed cracks in the optical micrographs. The inset in Figure 4(a, b, c and d) showed that the generated photonic crystal films are composed of several mono-layers, arranged in an ordered manner.

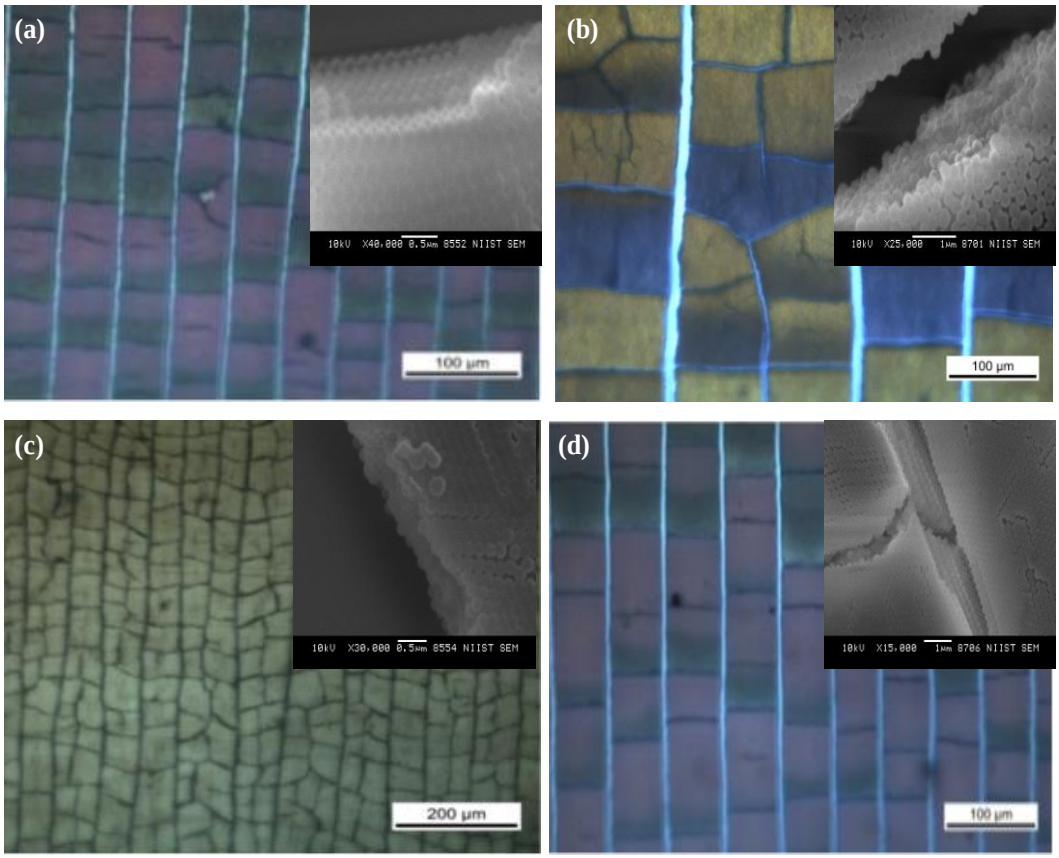


Figure 4: Optical electron micrographs with insets of scanning electron micrographs of the fabricated photonic crystals.

Atomic force microscopic analysis of photonic crystal films

The morphology of the fabricated photonic crystal films was viewed using an atomic force microscope in the tapping mode as shown by the two-dimensional AFM micrographs in Figure 5. The observed morphology is very similar to the impeccable closely-packed three-dimensional ordered hexagonal structure revealed by the scanning electron micrographs in Figure 3. The particles of the colloidal crystal films were observed to be spherical in shapes (Figure 5(a, b, c and c)).

The particle height/surface roughness/average particle diameters of the colloidal crystal particles were respectively observed to be 41 nm/ 9.24 nm /195 nm (Figure 5 (a)), 34 nm/ 7.44 nm/ 132 nm (Figure 5 (b)), 51 nm/ 10.51 nm/ 273 nm (Figure 5 (c)) and 38 nm/8.43 nm/ 160 nm (Figure 5 (c)). The average particle diameters estimated by the AFM analysis for the colloidal crystal films were also observed to be very close to the estimated particle diameter by the scanning electron microscopic analysis.

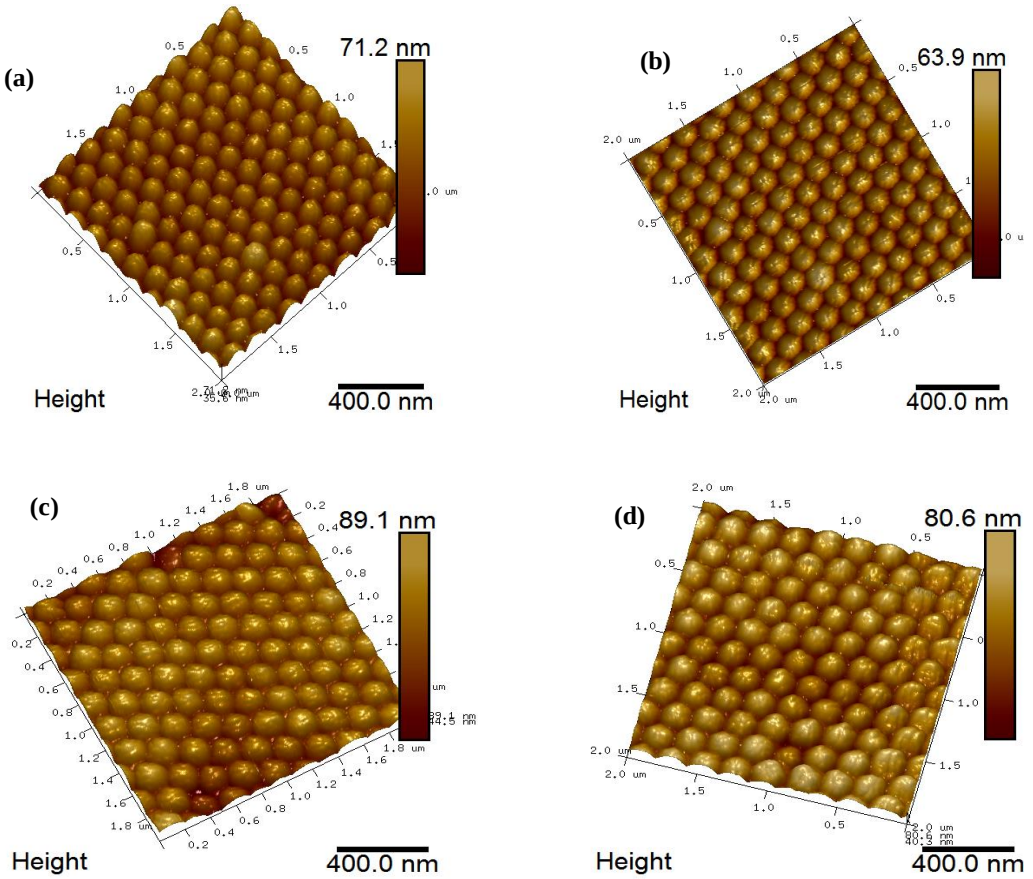


Figure 5: Two-dimensional atomic force micrographs of the fabricated colloidal films.

Conclusion

This study generated monochromatic coloured PCs with vivid colourations that are due to diffraction and scattering of light. The colour display characteristics were controlled by regulating the crystal lattice and periodicity of the colloidal crystal films. Microscopic analysis of the PCs films showed that the particles readily assemble themselves into an impeccable closely-packed three-dimensional ordered hexagonal structure with multiple monolayer arrangements. The high intensity and monochromatic nature of the colours may find use in optical sensing applications.

Competing Interests

The authors declare no conflicts of interest.

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