## Journal of Materials Chemistry

Cite this: J. Mater. Chem., 2012, 22, 24668

www.rsc.org/materials

### PAPER

# Highly ordered and gap controllable two-dimensional non-close-packed colloidal crystals and plasmonic-photonic crystals with enhanced optical transmission<sup>†</sup>

Zhongyu Cai,<sup>‡a</sup> Yan Jun Liu,<sup>‡b</sup> Eunice S. P. Leong,<sup>b</sup> Jinghua Teng<sup>\*b</sup> and Xianmao Lu<sup>\*a</sup>

*Received 24th July 2012, Accepted 28th September 2012* DOI: 10.1039/c2jm34896a

We present a facile one-step co-self-assembly method for the fabrication of two-dimensional (2D) nonclose-packed (ncp) colloidal crystals (CCs) using polystyrene (PS) colloidal spheres and tetraethylorthosilicate (TEOS) sol. The resultant 2D ncp CCs demonstrated long-range ordering at the centimeter-scale without cracks due to the addition of TEOS sol. The inter-particle gap of the ncp CCs can be easily controlled by varying the amount of TEOS sol added during the assembly process. The crack-free 2D CCs were employed to form hybrid plasmonic–photonic crystals by depositing a thin film of gold. Experimental and simulated transmission spectra of the hybrid plasmonic–photonic crystals were found to be in good agreement. This simple and low-cost method provides a platform for the fabrication of high-quality 2D ncp CCs and may facilitate the development of various applications of ncp CCs.

#### 1. Introduction

Non-close-packed (ncp) colloidal crystals (CCs) have attracted extensive interest in recent years for their fundamental and technological importance.<sup>1-3</sup> In comparison with close-packed CCs, ncp CCs can have a tunable inter-particle gap distance and a wider photonic band gap,<sup>4</sup> making them attractive materials for photonic devices such as optical switches,<sup>5</sup> all-optical chips,<sup>6</sup> and light-emitting diodes.<sup>7</sup> Two dimensional (2D) ncp CCs, in particular, have found applications in nanosphere lithography,8 tunable superhydrophobic surfaces,9 surface plasmonic devices,10 single quantum dot spectroscopy,<sup>11</sup> and edge-spreading lithography.<sup>12</sup> So far, 2D ncp CCs have been prepared via methods such as soft lithography,<sup>13,14</sup> controlled reactive ion etching,<sup>2,15</sup> electrostatics,<sup>16,17</sup> template-induced assembly,<sup>18-22</sup> optical tweezers,<sup>23,24</sup> and manipulation of dipole-dipole interaction.<sup>25,26</sup> However, these methods are limited by either high production cost or small fabrication area.

24668 | J. Mater. Chem., 2012, 22, 24668-24675

To achieve low-cost and large-area fabrication of 2D ncp CCs, a spin-coating method has been reported by Jiang *et al.*<sup>10,27</sup> In this method, the normal pressure produced by spin-coating and monomer photopolymerization squeezes particles against the substrates to form 2D ncp CCs. They further developed a universal templating method for the fabrication of wafer-scale 2D ncp colloidal crystals from various functional materials, without synthesizing uniform colloids of each material.<sup>28</sup> However, the resultant 2D CCs display a polycrystalline structure and a fixed interparticle gap. In addition, a priming of silicon wafer is necessary to avoid patch samples. To date, the fabrication of 2D ncp CCs with long-range ordering and single crystallinity still remains a challenge.

The self-assembly method, as an alternative strategy for the preparation of 2D ncp CCs, is attractive due to its cost-effectiveness and potential for large-area monocrystalline fabrication. It has been applied to the fabrication of highly ordered ncp CCs of hydrogel spheres in a relatively large domain.<sup>29,30</sup> In this approach, poly(N-isopropylacrylamide) (polyNIPAM) hydrogel spheres were self-assembled at the air-liquid interface into 2D highly crystalline domains by adding a certain amount of ethanol. Subsequently, a mechanical force is applied to merge the domains into monocrystalline areas in the range of square centimeters.<sup>30</sup> Though self-healing 2D ncp arrays in long-range ordering can be obtained by this method, additional apparatus (pressure-modulated nitrogen gun and spin-coater) and steps (oscillatory air stream and spin-coating) are needed. Additionally, the procedures are complicated and the quality of the resultant 2D ncp CCs is influenced by a number of factors such as spin coating speed and shear force, which considerably affect the

<sup>&</sup>lt;sup>a</sup>Department of Chemical and Biomolecular Engineering, National University of Singapore, 4 Engineering Drive 4, Singapore 117576. E-mail: chelxm@nus.edu.sg; Fax: +65 6779 1936; Tel: +65 6516 1071 <sup>b</sup>Institute of Materials Research and Engineering, Agency for Science, Technology and Research (A\*STAR), 3 Research Link, Singapore 117602. E-mail: jh-teng@imre.a-star.edu.sg; Fax: +65 6872 0785; Tel: +65 6874 8590

<sup>&</sup>lt;sup>†</sup> Electronic supplementary information (ESI) available: The FESEM images of 2D PS/SiO<sub>2</sub> CCs fabricated with different amounts of TEOS sol and 2D PS/SiO<sub>2</sub> CCs deposited with Au, the microscope image of 2D PS/SiO<sub>2</sub> CCs, and transmission spectra of the obtained 2D PS/SiO<sub>2</sub> CCs and a 50 nm thick gold film. See DOI: 10.1039/c2jm34896a <sup>‡</sup> These authors contributed to this work equally.

perfection of the structure. Recently, convective self-assembly<sup>31</sup> has attracted considerable interest due to its robustness and simplicity. Close-packed 2D CCs have been demonstrated using this method.<sup>22,32,33</sup> Yan *et al.* recently fabricated 2D binary CCs in a relatively large area using a co-self-assembly method.<sup>34</sup> However, 2D ncp CCs have not been directly fabricated using either a convective self-assembly or a co-self-assembly method.

Here we report a flexible and scalable approach based on a coself-assembly technique to fabricate monolayer ncp CCs. In this method, submicron polystyrene (PS) spheres dispersed in tetraethylorthosilicate (TEOS) sol are self-assembled to form 2D colloidal crystal–silica nanocomposite films. Crack-free 2D ncp CCs with a controllable inter-particle gap can be obtained due to the polymerization of TEOS sol during the self-assembly process. 2D hybrid plasmonic–photonic crystals with enhanced optical transmission were fabricated by depositing a thin film of gold onto the 2D ncp CCs. This facile co-self-assembly technique can significantly reduce crack density, leading to the formation of highly ordered ncp CCs in a large area.

#### 2. Experimental section

#### 2.1. Materials

All chemicals including styrene (99%, Aldrich), potassium persulfate (99%, Aldrich), ethanol (99.95%, Aldrich), sulfuric acid (98%, Merck), hydrogen peroxide (35%, Scharlau Chemie S.A.), TEOS (98%, Aldrich), and hydrochloric acid (37%, Sigma-Aldrich) were used as purchased. Microscope cover glasses (22 mm × 22 mm × 0.3 mm, Deckgläser) were used as substrates for the fabrication of crack-free PS CCs. The glass substrates were treated in a piranha solution (3 : 1 v/v, 98% H<sub>2</sub>SO<sub>4</sub>/35% H<sub>2</sub>O<sub>2</sub>) at 60 °C for 2 h before use. (*Caution! Piranha and the components of piranha are highly corrosive chemicals that present numerous health hazards. When* H<sub>2</sub>O<sub>2</sub> *and* H<sub>2</sub>SO<sub>4</sub> *are combined*, *an exothermic, potentially explosive reaction will result. Prior to working with piranha solutions, the reader is encouraged to take all necessary precautions.*)

#### 2.2. Preparation of 2D ncp PS/SiO<sub>2</sub> colloidal crystal films

The PS spheres were synthesized via an emulsifier-free emulsion polymerization method.<sup>35</sup> PS spheres with diameters of 277, 428, 715 and 1010 nm were used for the preparation of 2D PS CCs. The size deviations of all sizes of PS spheres are smaller than 2.5% except for the size of 715 nm (2.9%). The fabrication of ncp PS CCs was conducted in one step through co-self-assembly of PS/SiO<sub>2</sub> CCs by adding TEOS sol. In a typical process, 77.83 µL of a 4.02 vol% PS (428 nm in diameter) colloidal suspension (cleaned by centrifugation) was added to 20 mL of deionized water and 18.75 µL of TEOS sol. The TEOS sol consisting of a volume of TEOS, ethanol, and 0.10 M HCl with a ratio of 1:2:1, respectively, was stirred at room temperature for 1 h. The freshly prepared mixture was sonicated for 30 min before use. The glass substrates were then vertically suspended in the vial containing the colloid/TEOS suspension. The solvent content was evaporated at 65 °C slowly over a period of 24 h in an oven without disruption to allow the deposition of a thin film onto the suspended substrate.



Scheme 1 Schematic illustration of the fabrication procedures for generating monolayer ncp colloidal crystal–silica nanocomposites and hybrid plasmonic–photonic crystals.

#### 2.3. Fabrication of 2D ncp plasmonic-photonic crystals

The 2D ncp plasmonic–photonic crystals were formed by depositing a thin layer of Au onto the PS/SiO<sub>2</sub> CCs. Metal deposition was performed using an electron-beam evaporator (Explorer Coating System, Denton Vacuum). The working pressure during the evaporation was  $<5 \times 10^{-6}$  Torr. The temperature of the sample chamber was kept at 20 °C during the entire evaporation process, with the sample holder rotating at a rate of 50 rpm to ensure the uniformity of deposition. A 3 nm Cr adhesion layer and a 50 nm Au layer were subsequently deposited over the 2D PS/SiO<sub>2</sub> CC surface. Scheme 1 shows the illustration of the fabrication process of the 2D ncp CCs and the hybrid plasmonic–photonic crystals.

#### 2.4. Characterization

Scanning electron microscope (SEM) images of the 2D PS/SiO<sub>2</sub> CCs and the hybrid plasmonic–photonic crystals were recorded using a JEOL JSM-6700F field-emission SEM (FESEM). Atomic force microscope (AFM) imaging was performed on a Nanoscope Dimension 3100 system operating in tapping mode. Optical spectra were obtained on an UV-visible-NIR microspectrophotometer (CRAIC QDI 2010<sup>TM</sup>).

#### 2.5. FDTD simulation

The optical transmission properties were simulated using the finite-difference time-domain method (FDTD, Lumerical). A unit cell of the structure was simulated under periodic boundary conditions in the *x*- and *y*-direction and perfectly matched layer (PML) boundary conditions in the *z*-direction. The dispersion of gold was based on the Johnson and Christy model in the material library of the software. The structures were illuminated with a plane wave directed along the *z*-direction.

#### 3. Results and discussion

#### 3.1. Fabrication of 2D ncp CCs

Fig. 1a and b show low-magnification FESEM images of the 2D ncp  $PS/SiO_2$  CCs fabricated using PS spheres with a diameter of 428 nm. These images indicate that 2D ncp  $PS/SiO_2$  CCs can be fabricated in a relatively large domain without cracks (hundreds of micrometers). The larger domain can be observed at the centimetre scale under a microscope (Fig. S1†). A closer look of



Fig. 1 FESEM images of the 2D PS/SiO<sub>2</sub> CCs prepared *via* a co-self-assembly method using PS with sizes of (a–c) 428 nm, (d) 277 nm, and (e and f) 715 nm. The volume of TEOS sol was 20.25  $\mu$ L.

the CCs shows that the PS spheres are arranged with a uniform inter-particle gap (Fig. 1c). 2D ncp  $PS/SiO_2$  colloidal crystal films were also fabricated using PS spheres with diameters of 277 and 715 nm, as shown in Fig. 1d and e, respectively. The long-range ordering of all these samples with different particle sizes demonstrates the effectiveness of the co-self-assembly method. It is worth noting that the monodispersity of PS particles significantly affects the quality of 2D ncp CCs fabricated using this method. A few point defects were observed in the CCs fabricated using PS spheres with a diameter of 715 nm due to the larger

distribution of the particle size (size deviation is 2.9%) (Fig. 1f). But as indicated by the black circle in Fig. 1f, such a point defect in the PS lattice only leads to local distortion without propagating through the lattice. The occurrence of point defects may cause the nucleation of a domain with new orientation. However, with continued growth, this new domain orientation is gradually "corrected" to the original orientation before it finally disappears completely (as shown by the black arrow in Fig. 1f). For CCs made from highly monodispersed PS spheres (size deviation < 2.5%), polycrystallinity was not observed. In addition, this



Fig. 2 (a and b) Cross-sectional SEM images and (c and d) 3D and 2D AFM images of the PS/SiO<sub>2</sub> CCs fabricated using 428 nm PS and 20.25  $\mu$ L TEOS sol.

method is still valid for the fabrication of 2D ncp CCs with PS spheres larger than 1000 nm in diameter (Fig. S2<sup>†</sup>).

Cross-sectional SEM images of the 2D ncp CCs confirm that the CCs are monolayer and the PS spheres are embedded in silicate species (Fig. 2a and b). The atomic force microscope (AFM) measurement was carried out to further examine the quality of the 2D ncp CCs. As shown in Fig. 2c and d, the ncp CCs are highly ordered and the PS spheres are in the same plane, forming a monolayer on the substrate.

#### 3.2. Comparison between co-self-assembly and convective selfassembly methods

We also fabricated close-packed PS CCs using a convective selfassembly method under the same experimental conditions except that no TEOS sol was added. PS spheres with a diameter of 277 nm were used and the resulting PS CCs are compared with those obtained *via* a co-self-assembly method. Fig. 3a and b show the SEM images of 2D ncp CCs fabricated by a co-self-assembly method while Fig. 3c and d show the SEM images of closepacked CCs fabricated by a convective self-assembly method. For a co-self-assembly approach, well ordered and crack-free 2D ncp CCs can be fabricated in a relatively large area. In contrast, the close-packed CCs fabricated *via* a convective self-assembly method without adding TEOS sol exhibit many cracks and only small domains of ordered structure can be observed. The measured inter-crack distance is around 300 nm. In addition, the convective self-assembly leads to both local and long-range lattice distortions, while for the co-self-assembly method, the CCs can tolerate point defects and the lattice perturbation is only restricted to the neighbors.

Previous theoretical<sup>36-38</sup> and experimental<sup>39,40</sup> studies on the convective self-assembly indicate that formation of cracks is due to capillary stresses caused by both the drying front during the self-assembly stage and the removal of a residual solvent during the drying stage. Our co-self-assembly method in the fabrication of 2D ncp CCs without cracks is different due to the addition of TEOS sol. It is known that TEOS sol hydrolyzes during the selfassembly process under the catalysis of HCl. Therefore, in the coself-assembly of PS colloidal spheres mixed with TEOS sol, the sol-gel matrix that undergoes polycondensation provides a glue/ necking to the assembling PS spheres.<sup>41</sup> In this system, the formation of a 2D colloidal crystal and the associated interfaces that exist between the polymerizing TEOS sol-gel and the assembling PS colloidal spheres play a very important role in the fabrication of crack-free 2D colloidal crystal films. Firstly, the formation of a 2D colloidal crystal and the associated interfaces may provide sites for the relaxation of tensile stresses generated during the gelation process. Secondly, controlled solvent release during the polycondensation reaction can also occur at these interfaces and be channelled to evaporate at the surface.<sup>42</sup> Therefore, the causes for capillary stresses in a



Fig. 3 (a and b) PS non-close and (c and d) close-packed CCs fabricated with a co-self-assembly method and a convective self-assembly method using 277 nm PS spheres.

convective self-assembly are avoided in the co-self-assembly method. Moreover, the moderate evaporation rate of the solvent at the drying stage caused by the addition of TEOS sol may benefit for the formation of crack-free CCs as well.<sup>39</sup> Thus, the robust and interconnected silicate network in these composite films may prohibit the formation/propagation of cracks. In addition, this method avoids the coffee stain effect and results in uniform 2D ncp colloidal crystal films due to the synergetic effect of a complex gelation process, Marangoni flow and convecting the PS colloidal spheres to the air–liquid interface during selfassembly.<sup>31,43,44</sup>

Fig. 4a and b show the SEM images of ncp PS/SiO<sub>2</sub> (before HF etching) and ncp PS CCs (after HF etching), respectively. After HF etching, the centre-to-centre distance remains unchanged while the inter-particle gap becomes smaller because a part of each colloidal sphere is buried under the silicate species and the silicate species is higher than the centre of the PS colloidal spheres in unetched 2D ncp CCs (Fig. S3<sup>†</sup>). One of the most prominent features of the resulting 2D ncp CCs is that the interparticle gap can be controlled by varying the amount of TEOS sol added during the co-self-assembly process. When 18.75, 20.25, 21.75, 23.25 and 25  $\mu$ L of TEOS sol used, the average inter-particle gaps were 53, 67, 89, 100 and 120 nm, respectively (Fig. 4a, S4<sup>†</sup> and 4c). By plotting the inter-particle gap as a function of the volume of TEOS sol (Fig. 4d), we found that the

inter-particle gap increases approximately linearly with the increase of the amount of TEOS sol in the mixed colloidal suspension. This relationship provides a useful guide for designing ncp CCs with controlled inter-particle gaps for different applications. The facile one-step co-self-assembly method developed in this work can be used in the fabrication of large area, crack-free, long-range ordered 2D CCs. However, it should be noted that there exists a critical amount of TEOS sol in the mixed colloidal suspension. When the amount of TEOS sol exceeds 26.25  $\mu$ L (upper limit), an overlayer of SiO<sub>2</sub> will form on top of the 2D CCs and cover the PS spheres (Fig. S5a†). At the lower threshold (around 8.75  $\mu$ L), high-quality 2D ncp CCs cannot be obtained in a large area (Fig. S5b†).

#### 3.3. Fabrication of 2D hybrid plasmonic-photonic crystals

It has been reported that metal-coated CCs can exhibit extraordinary optical transmission,<sup>45–47</sup> which is crucial for plasmonic applications including biosensing, color filters, and metamaterials. Here we deposited a gold film on the 2D ncp CCs to form hybrid plasmonic–photonic crystals and investigated their optical transmission properties. Fig. 5 displays typical FESEM images of a 2D ncp CC (PS sphere size: 428 nm; TEOS sol: 18.75  $\mu$ L) before and after the deposition of a 50 nm thick gold film. It is clear that both the long-range ordering and the



Fig. 4 The inter-particle gap can be modulated by varying the amount of TEOS sol. FESEM images of PS/SiO<sub>2</sub> CCs (a) before and (b) after HF etching (18.75  $\mu$ L TEOS sol); (c) 2D ncp PS/SiO<sub>2</sub> CCs without etching (25  $\mu$ L TEOS sol) and (d) the inter-particle gap as a function of the volume of TEOS sol added in the mixed colloidal suspension.

centre-to-centre distance are well preserved after the Au deposition while the inter-particle gap reduces from 53 nm to 36 nm on average. A similar decrease in the inter-particle gap was also observed in other samples (Fig. S6<sup>†</sup>).

The optical transmission spectra and FDTD simulation results of the plasmonic-photonic crystals formed from Au-coated 2D

ncp CCs are shown in Fig. 6. The measured (Fig. 6a) and simulated spectra (Fig. 6b) are in good agreement in terms of the peak positions. Compared to the uncoated 2D ncp PS/SiO<sub>2</sub> CCs (see Fig. S7†), the hybrid plasmonic–photonic crystals display three optical transmission peaks. The peak at  $\sim$ 500 nm is associated with electron transition and recombination between the



Fig. 5 FESEM images of 2D ncp CCs made from 428 nm PS spheres with 18.75 µL TEOS sol (a) before and (b) after deposition of a 50 nm Au film.



**Fig. 6** (a) Measured and (b) simulated transmission spectra of the hybrid plasmonic–photonic crystals obtained by coating a 50 nm gold film on the 2D ncp CCs with different inter-particle gaps.

filled d-bands and the Fermi level in the conduction band of the gold film.<sup>48-50</sup> For the CCs with 53 nm gap, another two peaks at  $\sim$ 570 nm and  $\sim$ 720 nm arise from the surface plasmon polariton (SPP) modes. These two peaks are much stronger than the transmission spectrum from a 50 nm Au film on the silica substrate (Fig. S8<sup>†</sup>). For the 2D hexagonal lattice, the momentum match condition is  $k_{spp}(\omega) = k_0(\omega)\sin \theta \pm iG_x \pm$  $jG_{\nu}$ <sup>51</sup> where  $k_{\rm spp}(\omega) = (2\pi/\lambda)[\varepsilon_{\rm m}\varepsilon_{\rm d}/(\varepsilon_{\rm m} + \varepsilon_{\rm d})]^{1/2}$  with  $\varepsilon_{\rm m}$  and  $\varepsilon_{\rm d}$ being the dielectric constants of the metal and dielectric (PS opals or air) at the interface,  $k_0$  is the light wavevector at the incident angle of  $\theta$ ,  $G_x$  and  $G_y$  are Bragg vectors of the CCs, *i* and *j* are integers. From the above equations, the peaks at  $\sim$ 570 nm and  $\sim$ 720 nm can be assigned to the SPP modes that propagate along the air-gold and opal-gold interfaces, respectively. As the gap distance increases from 53 nm to 100 nm, these two peaks blueshifted to shorter wavelengths. It is noteworthy that the SPP resonance associated with the interfaces of the 2D ncp CCs can be tuned via the amount of TEOS sol added in the assembly process, while the SPP resonances are fixed for 2D close-packed CCs with the same sphere size.

#### 4. Conclusions

In summary, 2D ncp CCs were fabricated *via* a facile co-selfassembly method using PS colloidal spheres and TEOS sol. The size and inter-particle gap of the ncp CCs can be easily and precisely controlled by the amount of TEOS sol added in the process. These 2D ncp CCs were further employed to form hybrid plasmonic–photonic crystals by depositing a gold film on the crystals. The resonance peak can be tuned according to the inter-particle gap size. This fabrication approach is cost effective and able to fabricate highly ordered, crack-free 2D ncp CCs in a large area with high crystallinity. The high-quality 2D ncp CCs prepared *via* the co-self-assembly method may facilitate the applications of 2D CCs in nano-lithography and nano-photonics and plasmonics.

#### Acknowledgements

This work was supported by Ministry of Education Singapore under grant no. R279-000-298-112 and Agency for Science, Technology and Research (A\*STAR) under grant no. 0921540099 and 0921540098.

#### Notes and references

- 1 A. Yethiraj and A. van Blaaderen, Nature, 2003, 421, 513-517.
- 2 B. J. Y. Tan, C. H. Sow, K. Y. Lim, F. C. Cheong, G. L. Chong, A. T. S. Wee and C. K. Ong, *J. Phys. Chem. B*, 2004, **108**, 18575– 18579.
- 3 R. Fenollosa and F. Meseguer, Adv. Mater., 2003, 15, 1282-1285.
- 4 M. Doosje, B. J. Hoenders and J. Knoester, J. Opt. Soc. Am. B, 2000, 17, 600–606.
- 5 J. M. Weissman, H. B. Sunkara, A. S. Tse and S. A. Asher, *Science*, 1996, **274**, 959–963.
- 6 S.-Y. Lin, E. Chow, V. Hietala, P. R. Villeneuve and J. D. Joannopoulos, *Science*, 1998, **282**, 274–276.
- 7 E. Yablonovitch, J. Opt. Soc. Am. B, 1993, 10, 283-295.
- 8 A. Kosiorek, W. Kandulski, P. Chudzinski, K. Kempa and M. Giersig, *Nano Lett.*, 2004, 4, 1359–1363.
- 9 J. T. Han, D. H. Lee, C. Y. Ryu and K. Cho, J. Am. Chem. Soc., 2004, 126, 4796–4797.
- 10 P. Jiang and M. J. McFarland, J. Am. Chem. Soc., 2005, 127, 3710– 3711.
- 11 U. Håkanson, et al., Nanotechnology, 2003, 14, 675.
- 12 J. M. McLellan, M. Geissler and Y. Xia, J. Am. Chem. Soc., 2004, 126, 10830–10831.
- 13 X. Yan, J. Yao, G. Lu, X. Li, J. Zhang, K. Han and B. Yang, J. Am. Chem. Soc., 2005, 127, 7688–7689.
- 14 X. Li, T. Wang, J. Zhang, X. Yan, X. Zhang, D. Zhu, W. Li, X. Zhang and B. Yang, *Langmuir*, 2009, **26**, 2930–2936.
- 15 D.-G. Choi, H. K. Yu, S. G. Jang and S.-M. Yang, J. Am. Chem. Soc., 2004, 126, 7019–7025.
- 16 J. Aizenberg, P. V. Braun and P. Wiltzius, *Phys. Rev. Lett.*, 2000, 84, 2997.
- 17 A. Pertsinidis and X. S. Ling, Phys. Rev. Lett., 2001, 87, 098303.
- 18 Y. Yin, Y. Lu, B. Gates and Y. Xia, J. Am. Chem. Soc., 2001, 123, 8718–8729.
- 19 R. E. Schaak, R. E. Cable, B. M. Leonard and B. C. Norris, Langmuir, 2004, 20, 7293–7297.
- 20 Y. Xia, Y. Yin, Y. Lu and J. McLellan, Adv. Funct. Mater., 2003, 13, 907–918.
- 21 S. Koh, Nanoscale Res. Lett., 2007, 2, 519-545.
- 22 Z. Cai, J. Teng, D. Xia and X. S. Zhao, J. Phys. Chem. C, 2011, 115, 9970–9976.
- 23 J. P. Hoogenboom, D. L. J. Vossen, C. Faivre-Moskalenko, M. Dogterom and A. v. Blaaderen, *Appl. Phys. Lett.*, 2002, 80, 4828–4830.
- 24 D. G. Grier, Nature, 2003, 424, 810-816.
- 25 W. D. Ristenpart, I. A. Aksay and D. A. Saville, *Phys. Rev. Lett.*, 2003, **90**, 128303.

- 26 S. O. Lumsdon, E. W. Kaler, J. P. Williams and O. D. Velev, *Appl. Phys. Lett.*, 2003, **82**, 949–951.
- 27 P. Jiang, T. Prasad, M. J. McFarland and V. L. Colvin, *Appl. Phys. Lett.*, 2006, **89**, 011908.
- 28 S. Venkatesh, P. Jiang and B. Jiang, *Langmuir*, 2007, 23, 8231–8235.
- 29 G. Zhang, D. Wang, Z.-Z. Gu, J. Hartmann and H. Möhwald, *Chem. Mater.*, 2005, **17**, 5268–5274.
- 30 S. B. Quint and C. Pacholski, Soft Matter, 2011, 7, 3735–3738.
- 31 A. S. Dimitrov and K. Nagayama, Langmuir, 1996, 12, 1303-1311.
- 32 B. G. Prevo and O. D. Velev, Langmuir, 2004, 20, 2099-2107.
- 33 M. H. Kim, S. H. Im and O. O. Park, *Adv. Funct. Mater.*, 2005, **15**, 1329–1335.
- 34 J. Yu, Q. Yan and D. Shen, ACS Appl. Mater. Interfaces, 2010, 2, 1922–1926.
- 35 Z. Cai, J. Teng, Q. Yan and X. S. Zhao, *Colloids Surf.*, A, 2012, **402**, 37–44.
- 36 E. R. Dufresne, E. I. Corwin, N. A. Greenblatt, J. Ashmore, D. Y. Wang, A. D. Dinsmore, J. X. Cheng, X. S. Xie, J. W. Hutchinson and D. A. Weitz, *Phys. Rev. Lett.*, 2003, **91**, 224501.
- 37 W. P. Lee and A. F. Routh, Langmuir, 2004, 20, 9885-9888.
- 38 E. R. Dufresne, D. J. Stark, N. A. Greenblatt, J. X. Cheng, J. W. Hutchinson, L. Mahadevan and D. A. Weitz, *Langmuir*, 2006, 22, 7144–7147.
- 39 F. Zeng, Z. Sun, C. Wang, B. Ren, X. Liu and Z. Tong, *Langmuir*, 2002, 18, 9116–9120.

- 40 S.-L. Kuai, X.-F. Hu, A. Haché and V.-V. Truong, J. Cryst. Growth, 2004, 267, 317–324.
- 41 Z. Cai, J. Teng, Y. Wan and X. S. Zhao, J. Colloid Interface Sci., 2012, 380, 42–50.
- 42 C. J. Brinker and G. W. Scherer, *Sol-Gel Science: The Physics and Chemistry of Sol-Gel Processing*, Academic Press, Inc., New York, 1990.
- 43 N. Vogel, C. K. Weiss and K. Landfester, Soft Matter, 2012, 8, 4044– 4061.
- 44 M. Majumder, C. S. Rendall, J. A. Eukel, J. Y. L. Wang, N. Behabtu, C. L. Pint, T.-Y. Liu, A. W. Orbaek, F. Mirri, J. Nam, A. R. Barron, R. H. Hauge, H. K. Schmidt and M. Pasquali, *J. Phys. Chem. B*, 2012, 116, 6536–6542.
- 45 P. Zhan, Z. L. Wang, H. Dong, J. Sun, J. Wu, H. T. Wang, S. N. Zhu, N. B. Ming and J. Zi, *Adv. Mater.*, 2006, **18**, 1612–1616.
- 46 L. Landström, D. Brodoceanu, D. Bäuerle, F. J. Garcia-Vidal, S. G. Rodrigo and L. Martin-Moreno, *Opt. Express*, 2009, **17**, 761– 772.
- 47 S. G. Romanov, A. V. Korovin, A. Regensburger and U. Peschel, *Adv. Mater.*, 2011, 23, 2515–2533.
- 48 A. Mooradian, Phys. Rev. Lett., 1969, 22, 185-187.
- 49 G. T. Boyd, Z. H. Yu and Y. R. Shen, Phys. Rev. B: Condens. Matter Mater. Phys., 1986, 33, 7923–7936.
- 50 M. Xiao and N. Rakov, Phys. Lett. A, 2003, 309, 452-456.
- 51 H. F. Ghaemi, T. Thio, D. E. Grupp, T. W. Ebbesen and H. J. Lezec, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1998, 58, 6779–6782.