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Large-Scale Colloidal Self-Assembly by Doctor Blade Coating

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This article reports a simple, roll-to-roll compatible coating technology for producing 3D highly ordered colloidal crystal-polymer nanocomposites, colloidal crystals, and macroporous polymer membranes. A vertically beveled doctor blade is utilized to shear align silica microsphere-monomer suspensions to form large-area nanocomposites in a single step. The polymer matrix and the silica microspheres can be selectively removed to create colloidal crystals and selfstanding macroporous polymer membranes. The thickness of the shear-aligned crystal is correlated with the viscosity of the colloidal suspension, and the coating speed and the correlations can be qualitatively explained by adapting the mechanisms developed for conventional doctor blade coating. We further demonstrate that the doctor blade coating speed can be significantly increased by using a dual-blade setup. The optical properties of the self-assembled structures are evaluated by normal-incidence reflection measurements, and the experimental results agree well with the theoretical predictions using Bragg's law and a scalar wave approximation model. We have also demonstrated that the templated macroporous polymers with interconnected voids and uniform interconnecting nanopores can be directly used as filtration membranes to achieve size-exclusive separation of particles.

Introduction

The spontaneous crystallization of monodisperse colloidal particles is of considerable technological importance and great scientific interest in developing diffractive optical devices,^{1–3} chemical and biological sensors,^{4–7} full-color displays,^{8–11} ultrahigh-density optical and magnetic recording media,^{12,13} and model systems for fundamental studies of crystallization, melting, and relaxation.^{14–18} The self-assembled colloidal arrays have also been extensively exploited as a template for creating a wide spectrum of functional periodic structures, such as macroporous photonic crystals with full photonic band gaps,^{19,20} periodic metal

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nanostructures as surface-enhanced Raman scattering substrates,²¹⁻²⁶ biomimetic antireflection coatings for highly efficient solar cells,^{27,28} and separation media for macromolecules and DNA separation.^{29,30} Highly ordered colloidal crystal–polymer nanocomposites that have important technological applications ranging from photonic paper and displays to optical storage media and security data encryption can be prepared by filling the interstitials between the self-assembled colloidal arrays.31,32

A large variety of methodologies, including gravitational sedi-mentation,³³ capillary-force-induced self-assembly,^{19,34–36} electro-static repulsion,^{5,37,38} physical confinement,^{39,40} electric- and magnetic-field-assisted assembly,^{11,41–43} and shear-force-induced ordering,^{17,44–51} have been developed to create high-quality

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Figure 1. Schematic illustration of the experimental setup for assembling large-area colloidal crystal-polymer nanocomposites by using a simple doctor blade coating technique.

colloidal crystals. Unfortunately, most of the available colloidal self-assembly technologies are favorable only for low-volume, laboratory-scale production. It usually takes hours to days to create a centimeter-sized crystal. Technical incompatibility with mature microfabrication is another major issue for current colloidal self-assemblies. These issues greatly impede the economic and large-scale production of practical devices and therefore need to be addressed before bottom-up colloidal self-assembly reaches its full potential.

To resolve the scale-up and compatibility issues of current colloidal self-assembly, a spin-coating technology has recently been developed.^{14,44,45,52} The methodology is based on shear aligning concentrated colloidal suspensions by using standard spin-coating equipment. Spin-coating enables the rapid production of wafer-sized colloidal arrays with remarkably large domain sizes and unusual non-close-packed structures.^{45,52} However, this scalable technology is still a batch process. For industrial-scale mass production, a roll-to-roll compatible, continuous process is highly desired. Additionally, the shear force direction changes circularly in the spin-coating process. This leads to the formation of six-arm diffraction patterns on the sample surface,^{45,52} impeding many optical applications (e.g., displays and optical filters) that require a uniform diffractive color.

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Doctor blade coating (DBC) is widely used in the textile, paper, photographic film, printing, and ceramic industries to create highly uniform flat films over large areas. $^{53-57}$ In DBC, an immobilized blade applies a unidirectional shear force to a slurry that passes through a small gap between the blade and the substrate. This process is roll-to-roll compatible and has played a crucial role in ceramic processing to produce thin, flat ceramic tapes for dielectrics, fuel cells, batteries, and functionally graded materials.⁵³ Velev et al. developed a simplified DBC process,⁵⁸ which originated from an evaporative colloidal assembly technology,^{59–61} to create colloidal crystals with thickness ranging from a monolayer to a few layers. Capillary force is the major driving force for colloidal crystallization in this process. Inspired by this technology, we here report a roll-to-roll compatible DBC technology for producing highly ordered colloidal crystalpolymer nanocomposites, colloidal crystals, and macroporous polymer membranes. The resulting 3D ordered structures exhibit uniform diffractive colors. Most importantly, we demonstrate that the templated macroporous membranes with interconnected voids and uniform interconnecting nanopores can be directly used as filtration membranes to achieve the size-exclusive separation of particles.

Experimental Section

Materials and Substrates. All solvents and chemicals were of reagent quality and were used without further purification. Ethanol (200 proof) was purchased from Pharmaco Products. Ethoxylated trimethylolpropane triacrylate monomer (ETPTA,

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Figure 2. Colloidal crystal–polymer nanocomposites fabricated by the doctor blade coating technique. (A) Photograph of a multilayer nanocomposite consisting of 290 nm silica spheres embedded in an ETPTA matrix coated onto a glass substrate. (B) Top-view SEM image of the sample in A. Inset showing a Fourier transform of a $40 \,\mu m \times 40 \,\mu m$ region. (C) Magnified SEM image of B. (D) Pair correlation function (PCF) calculated from the SEM image in B. For comparison, the PCF for an ideal lattice with hexagonal close-packed structure is also shown (black lines). (E) Top-view SEM image of a sample consisting of 330 nm silica spheres embedded in an ETPTA matrix. (F) Top-view SEM image of a nanocomposite consisting of 290 nm silica spheres embedded in a PEGDA matrix. All samples were prepared by DB coating 50 vol % colloidal suspensions at a speed of 0.1 μ m/s.

SR 454) was obtained from Sartomer. Photoinitiator Darocur 1173 (2-hydroxy-2-methyl-1-phenyl-1-propanone) was provided by Ciba-Geigy. Silicon wafers (test grade, n type, Wafernet) and glass microslides (Fisher) were cleaned in piranha solution (a 3:1 mixture of concentrated sulfuric acid and 30% hydrogen peroxide) for half an hour, rinsed with Milli-Q water (18.2 M Ω cm), and dried in a stream of nitrogen.

Instrumentation. Scanning electron microscopy (SEM) was carried out on a JEOL 6335F FEG-SEM. A thin layer of gold was sputtered onto the samples prior to imaging. Transmission

electron microscopy (TEM) was performed on a JEOL 200CX TEM. Photopolymerization of the ETPTA monomer was carried out on a pulsed UV curing system (RC 742, Xenon). A KD Scientific 780-230 syringe pump was used to control the coating speed precisely. The viscosity of colloidal suspensions was measured using an ARESLS-1 rheometer (TA Instruments). Oxygen plasma etching was performed on a Unaxis Shuttlelock RIE/ICP reactive-ion etcher. Normal incidence optical reflection spectra were obtained using an Ocean Optics HR4000 high-resolution fiber optic vis-near-IR spectrometer with a reflection probe.



Figure 3. Thickness dependence of the DB-coated colloidal crystal— ETPTA nanocomposites on the coating speed and particle volume fraction for (A) 290, (B) 330, and (C) 560 nm silica spheres.

Optical transmission measurements of gold nanoparticle solutions were carried out on a ThermoSpectronic Genesys 10 UV-vis spectrometer.

Preparation of Colloidal Suspensions

The synthesis of monodisperse silica microspheres with less than 5% diameter variation was performed by following the wellestablished Stöber method.⁶² The purified silica microspheres (by multiple centrifugation/redispersion cycles in 200 proof ethanol) were redispersed in ETPTA monomer using a Thermolyne vortex mixer. Darocur 1173 (2 wt %) was added as the photoinitiator.



Figure 4. Schematic illustration of the velocity profile and the pressure head (Δh) in the doctor blade coating process.



Figure 5. Relative viscosity of 330 nm silica spheres/ETPTA suspensions with different particle volume fractions at various shear rates.



Figure 6. Cross-sectional SEM image of a silica colloidal crystal after removing the ETPTA matrix by 10 min of oxygen plasma etching.

The final particle volume fraction of colloidal suspensions was adjusted from 20 to 50%. After filtration through a 5 μ m syringe filter (Whatman) to remove any large particles, the transparent

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Figure 7. Macroporous polymer membrane after the selective removal of templating silica spheres. (A) Photograph of a free-standing, macroporous ETPTA film templated from 290 nm silica spheres. (B) Top-view SEM image of the sample in A. (C) Magnified SEM image of B. (D) Cross-sectional SEM image of the sample in A. The sample was coated at a speed of $5 \mu m/s$.

viscous solution was stored in an open vial in the dark overnight to allow any residual ethanol to evaporate.

Doctor Blade Coating. An immobilized 90°-beveled razor blade (Fisher, 4 cm wide) was gently placed on a substrate. One milliliter of the above silica–ETPTA suspension was dispensed along one sidewall of the blade onto the substrate. The substrate was dragged by a syringe pump at a controlled speed. The blade could then spread the colloidal suspension uniformly on the substrate. After DBC, the sample was transferred to a pulsed UV curing system and ETPTA monomer was rapidly polymerized by exposure to UV radiation for 4 s. The polymer matrix could be removed by using a reactive ion etcher operating at 40 mTorr oxygen pressure, a 40 sccm flow rate, and 100 W for 10 min. To prepare macroporous polymers, the silica–ETPTA nanocomposites were immersed in a 2 vol % hydrofluoric acid aqueous solution for 30 min, then rinsed with DI water, and finally dried in a stream of nitrogen.

Relative Viscosity Measurements. Experiments were performed using 50-mm-diameter parallel-plate geometry to characterize the rheological properties of the colloidal suspensions under shear. The gap between plates was set to 500 μ m in all experiments. To ensure that each test began from a similar initial state, the suspensions were presheared at a rate of 100 s^{-1} for 300 s, which was sufficient to enable the suspension to reach a steady state. The temperature was maintained at 25 °C, and the temperature fluctuation was less than 0.05 °C during a typical test.

Normal Incidence Optical Reflection Measurements. An Ocean Optics spectrometer with a reflection probe was used for reflectance measurements. A calibrated halogen light source was used to illuminate the sample. The beam spot size was about 3 mm on the sample surface. Measurements were performed at normal incidence, and the cone angle of collection was less than 5°. Absolute reflectivity was obtained as a ratio of the sample spectrum to the reference spectrum. The reference spectrum was the optical density obtained from an aluminum-sputtered (1000 nm thick) silicon wafer. The final value of the absolute reflectivity was the average of several measurements obtained from different spots on the sample surface.

Results and Discussion

The schematic illustration of the DBC process for fabricating 3D highly ordered colloidal crystal-polymer nanocomposites is shown in Figure 1. Monodisperse silica microspheres synthesized by the Stöber method are first dispersed in a nonvolatile monomer, ethoxylated trimethylolpropane triacrylate (ETPTA, M.W. 428, viscosity 60 cps), with 2 wt % Darocur 1173 as the photoinitiator. The particle volume fraction is adjusted from 20 to 50%. The resulting colloidal suspensions are transparent because of refractive index (RI) matching between silica microspheres (RI ~1.42) and ETPTA monomer (RI ~1.46). The electrostatic repulsion between silica microspheres (zeta potential of ca. -45 mV in ETPTA)⁶³ stabilizes the suspensions for at least a few weeks. The suspensions are then dispensed along a sidewall of an immobilized,

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Figure 8. (A) Normal incidence optical reflection spectra of an ETPTA-silica colloidal crystal nanocomposite, a corresponding macroporous ETPTA film, and a released silica colloidal crystal with 290 nm spheres and 12 colloidal layers. The arrows indicate the expected positions of the peaks for each sample, calculated using Bragg's law at normal incidence. (B) Comparison of the experimental and SWA-simulated optical reflection spectra at normal incidence from a macroporous ETPTA film templated from 290 nm silica spheres.

vertically beveled razor blade that gently touches a substrate. A large variety of substrates, including glass microslides, silicon wafers, and plastic plates, can be used. The substrate is then dragged by a syringe pump at a controlled speed ranging from $\sim 0.1 \,\mu$ m/s to $> 1 \,$ mm/s. The razor blade offers a uniform shear force for aligning the suspended silica colloidal microspheres. The ETPTA monomer is finally photopolymerized by exposure to ultraviolet radiation to form 3D highly ordered colloidal crystal—polymer nanocomposites.

Figure 2A shows a photograph of a multilayer silica colloidal crystal–ETPTA nanocomposite consisting of 290 nm silica microspheres on a glass substrate illuminated with white light. The sample was prepared by DB coating a 50 vol % suspension at 0.1 μ m/s. It exhibits a uniform red color caused by Bragg diffraction of visible light from the crystalline lattice. The long-range ordering of silica microspheres is clearly evident from the typical top-view SEM image as shown in Figure 2B. The hexagonally arranged sharp peaks in the Fourier transform of a low-magnification SEM image (inset of Figure 2B) further confirm the long-range hexagonal order. Common defects, such as point vacancies and misaligned lines that are caused mostly by dust particles and silica microspheres with extreme sizes, are also apparent in the SEM image. The polymer matrix surrounding the silica microspheres is clearly seen from the magnified top-view

SEM image in Figure 2C. The interparticle distance of the colloidal crystal is calculated by the pair correlation function (PCF, Figure 2D), g(r), which is obtained from a low-magnification image such as that in Figure 2B as

$$g(r) = \frac{1}{\langle \rho \rangle} \frac{\mathrm{d}n(r, r + \mathrm{d}r)}{\mathrm{d}a(r, r + \mathrm{d}r)}$$

where $\langle \rho \rangle$ is the average particle number density and *r* is the particle radius. Figure 2D shows that the positions of the oscillating PCF peaks agree well with those obtained from a perfect hexagonal close-packed lattice.

DBC technology can be utilized to align uniform silica microspheres with diameters ranging from ~ 200 to ~ 700 nm, which can be easily synthesized by the Stöber method.^{62,64} Figure 2E shows a top-view SEM image of a nanocomposite consisting of 330 nm silica microspheres. The protrusion depth of 330 nm microspheres from the polymer matrix is apparently shallower than that of 290 nm spheres. This leads to the non-close-packed appearance of the microspheres as shown in Figure 2E. Indeed, extensive PCF calculations reveal that the DB-coated colloidal crystals are closepacked. To evaluate the minimal particle size that still allows the formation of highly ordered nanocomposites using DBC, we tested 70 nm silica spheres synthesized by microemulsion technology.65,66 However, only disordered arrays resulted. As demonstrated in our previous spin-coating technology, a nearly 1 order of magnitude higher shear rate is required to align 70 nm silica spheres compared to that required to align 300 nm particles.⁶³ Besides ETPTA, a large variety of nonvolatile monomers and monomer mixtures can also be used to form highly ordered colloidal crystal-polymer nanocomposites by DBC, provided the concentrated silica-monomer suspensions are stable. Figure 2F shows a top-view SEM image of a nanocomposite consisting of 290 nm silica spheres and a hydrophilic poly(ethylene glycol) (600) diacrylate (PEGDA, SR 610, Sartomer) matrix. The long-range ordering of the silica microspheres is similar to that of colloidal crystals prepared in other polymer matrixes.

Crystalline thickness is another important parameter in determining the quality and application of self-assembled crystals. We therefore conducted systematic investigations on the effect of coating speed, particle size, and particle volume fraction on the resulting nanocomposite thickness. The results are summarized in Figure 3 for silica microspheres of 290, 330, and 560 nm diameter. To obtain the average thickness and standard deviation, at least 3 samples were prepared under each condition and the crystal thicknesses at more than 10 random locations on each sample were measured by cross-sectional SEM. The crystalline quality of the sample was also monitored by SEM, and the data points in Figure 3 indicated only the conditions under which highly ordered nanocomposites were obtained. By analyzing the results in Figure 3, we found that (1) the nanocomposite becomes thicker when the coating speed increases; (2) the more dilute colloidal suspensions lead to thicker nanocomposites when the particle size and the coating speed remain the same; (3) larger particles lead to thicker samples when the particle volume fraction and the coating speed are the same; and (4) the operating window for obtaining highly ordered nanocomposites is narrower for the more dilute colloidal suspensions.

The above observations can be qualitatively explained by adapting the mechanisms developed for traditional DBC.^{54–57}

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Figure 9. Separation of 10 nm gold nanoparticles from 330 nm silica spheres by using a free-standing, macroporous ETPTA membrane filter. (A) Experimental setup. (B) Photograph of the gold nanoparticle/silica sphere solution prior to filtration. (C) Photograph of the solution after filtration. (D) TEM image of the solution in B. (E) TEM image of the solution in C.

In traditional DBC, both pressure-driven flow and shear-driven flow play a crucial role in determining the properties of the resulting coatings. Pressure-driven flow is caused by the pressure exerted by the colloidal suspension head, $\Delta P = \rho_{\text{suspensiong}}\Delta h$, where Δh is the height difference between the suspension reservoir and the DB-coated film (Figure 4).⁵⁷ A higher pressure head leads to a greater flow rate across the blade. Shear-driven flow is attributed to the movement of the substrate, and the corresponding shear stress (τ) can be evaluated by using Newton's law of viscosity (for Newtonian fluids)

$$\tau = -\mu \, \frac{\mathrm{d} v_x}{\mathrm{d} y}$$

where μ is the viscosity of colloidal suspension and v_x is the substrate velocity along the x direction.⁶⁷ As demonstrated in our

previous work, the concentrated silica–ETPTA suspension is Newtonian over four decades of shear rate.⁶³ In a Newtonian fluid, the flow rates originating from the pressure head and the shear drag force are additive.⁵⁴

We attribute the observed colloidal crystallization in the above DBC procedures to shear-induced ordering.¹⁷ Highly ordered colloidal arrays form when the shear rate is sufficiently high. To evaluate the critical shear rate needed to align colloidal particles, we measured the relative viscosity (normalized by the viscosity of the monomer, ~60 cps for ETPTA) of silica-monomer suspensions with different particle volume fractions at various shear rates (Figure 5). The obvious shear-thinning behavior is caused by the shear-induced crystallization of colloidal particles and the reduced resistance when layers of ordered spheres glide over one another.^{17,49} From Figure 5, it is apparent that a critical shear rate of ~10 s⁻¹ is needed to achieve the relative viscosity plateau. In our DBC procedures, the shear rate caused by the substrate drag alone is only ~0.1 s⁻¹ by using a typical substrate velocity

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Figure 10. (A) Comparison of the extinction spectra of the solutions in Figure 9B,C. (B) Calibration curve for calculating the concentration of gold nanoparticles in filtrate solutions.

 $(\sim 1 \,\mu$ m/s) and film thickness $(\sim 10 \,\mu$ m). Therefore, we deduce that the pressure-driven flow plays a more important role in determining the properties of the resulting films.

In our DBC setup (Figure 4), the pressure head drives the flow of the colloidal suspensions across the small gap ($< 1 \mu m$) between the blade and the substrate. The resulting film thickness is determined by this pressure and the suspension viscosity. A higher pressure and a lower viscosity lead to thicker films. From extensive experiments, we found that the suspension reservoir height was controlled by the coating speed: a faster substrate velocity led to a more rapid accumulation of colloidal suspensions. This results in a higher pressure head and thus a thicker film, agreeing with observation 1 above. For a given particle size and coating speed, our experimental results in Figure 5 show that the viscosities of the relatively dilute suspensions (35 and 20 vol %) are less than that of the 50 vol % suspension. Therefore, it is not surprising to observe the formation of thicker films for the more dilute colloidal suspensions (observation 2). Observation 3 above is also related to the viscosity of colloidal suspensions. Our previous results show that suspensions consisting of large silica particles exhibit a lower viscosity than do suspensions of smaller particles with the same particle volume fraction.⁶³ To explain observation 4, both suspension viscosity and shear rate effects need to be considered. From Newton's law of viscosity, the shear stress is proportional to the suspension viscosity and the shear rate. For a more dilute suspension, the lower suspension viscosity and the thicker final films (i.e., a smaller shear rate) contribute synergistically to a smaller shear stress. Thus, it is reasonable to observe the narrower operating window for obtaining highly ordered nanocomposites for the more dilute suspensions. A detailed rheological study and an analytical fluid flow model are being developed and the results will be reported in our future publications.

The polymer matrix of the shear-aligned nanocomposites can be selectively removed by oxygen plasma etching to release the embedded silica colloidal crystals. Figure 6 shows a cross-sectional SEM image of a colloidal crystal prepared by etching a nanocomposite sample at 40 mTorr oxygen pressure, a 40 sccm flow rate, and 100 W for 10 min. The long-range hexagonal ordering of the original nanocomposite is mostly retained in the final silica colloidal crystal, though some structural collapse during the polymer removal process is also noticed. This collapse makes the determination of the crystalline ordering and structure perpendicular to the substrate surface difficult. We therefore selectively etched out silica particles in the nanocomposites by a brief hydrofluoric acid (2 vol %) wash to create macroporous polymers. The structure does not collapse during the etching process, and the resulting film is easy to break to reveal the cross-section of the crystal. Figure 7A shows a photograph of a free-standing macroporous ETPTA membrane templated from 290 nm silica spheres. The film exhibits a striking green color caused by the Bragg diffraction of visible light from the crystalline lattice of air cavities in the polymer. The typical SEM image of the top surface of a macroporous film and the Fourier transform of a lowermagnification image as shown in Figure 7B reveals that the longrange hexagonal ordering of the shear-aligned nanocomposite is well retained during the wet-etching process. A magnified SEM image in Figure 7C also shows that the large voids templated from silica microspheres are interconnected through smaller pores that originate from the touching sites of silica particles in the nanocomposites.^{20,68} Extensive SEM characterizations confirm that the bottom side of the macroporous film has the same structure as the top surface. The crystalline ordering perpendicular to the (111) plane is clearly seen from the cross-sectional SEM image in Figure 7D. However, a detailed SEM analysis shows that no relationship between neighboring layers (e.g., ABCABC... for a face-centered cubic crystal or ABABAB... for a hexagonal close-packed crystal) can be obtained. This suggests that the hexagonal close-packed layers are randomly stacked. Indeed, random stacking has been commonly observed in selfassembled colloidal crystals prepared by gravitational sedimenta-tion and shear alignment.^{51,69}

To evaluate the optical properties and the crystalline structure of the DB-coated crystals further, we measured the optical reflection at normal incidence using an Ocean Optics vis-near-IR spectrometer with a reflection probe. Figure 8A shows the reflection spectra obtained from a nanocomposite consisting of 290 nm silica spheres and an ETPTA matrix and the corresponding silica colloidal crystal and macroporous ETPTA film. The samples were prepared by DBC at a speed of 0.1 μ m/s, and the film thickness was measured to be 12 ± 1 monolayers by SEM. All three spectra show distinct peaks caused by the Bragg diffraction of visible and near-IR light from the 3D ordered structures. The low refractive index contrast of the nanocomposite and the partially collapsed structure of the silica colloidal crystal lead to the low reflection amplitudes of the corresponding spectra. The position of the diffraction peak can be correlated to the sphere size and the effective refractive index of the medium (n_{eff}) using Bragg's law: $\lambda_{\text{peak}} = 2n_{\text{eff}}d\sin\theta$, where d is the interlayer spacing

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Figure 11. (A) Schematic illustration of the dual-blade setup. (B) Photograph of a multilayer nanocomposite consisting of 290 nm silica spheres embedded in an ETPTA matrix aligned by a dual-blade system at a coating speed of 1 mm/s.

and $\sin \theta = 1$ at normal incidence. The effective refractive index of the medium is calculated using $n_{eff} = n_1 f_1 + n_2 f_2$, where n_1 and n_2 are the refractive indices of the components and f_1 and f_2 are their corresponding volume fractions. Figure 8A shows that the predicted peak positions as indicated by the arrows agree well with the experimental results. We have also conducted a more rigorous full-spectrum calculation using a scalar wave approximation (SWA) model.⁷⁰ The calculated reflection spectrum from a macroporous ETPTA membrane with close-packed 290 nm voids and 12 monolayers is compared with the experimental spectrum in Figure 8B. The remarkable agreement between theory and experiment further confirms the highly crystalline quality of the shear-aligned crystals and the faithful replication of the original nanocomposite during HF treatment.

Besides straightforward optical applications, the templated macroporous membranes with open and interconnected voids can be directly used as size-exclusive filtration membranes for separating particles and other substances. Compared to common filtration membranes, such as track-etched polymer films and fiber-based membranes, the uniform size of the interconnecting nanopores and the high porosity of the templated macroporous polymers could enable more accurate fractionation of particulates and a higher flow rate. To evaluate the separation efficiency of the templated macroporous films, we conducted a simple proof-of-concept experiment using a separation apparatus as shown in Figure 9A. A 3-cm-diameter macroporous ETPTA membrane templated from 290 nm silica spheres was used as the filter. The size of the interconnecting pores was estimated to be \sim 50 nm by

SEM. The testing solution was prepared by mixing ~10 nm gold nanoparticles (0.01 vol %) prepared by a chemical reduction method^{71,72} and 330 nm silica microspheres (0.01 vol %) in ethanol. The resulting mixture is turbid (Figure 9B) because of random light scattering from 330 nm silica particles. The solution can easily pass through the macroporous polymer membrane even without applying a pressure or a vacuum. The filtrate solution is transparent and shows a red color (Figure 9C) caused by the distinctive surface plasmon resonance absorption of light by Au nanoparticles (Figure 10A). The complete removal of large silica microspheres is further confirmed by the TEM images in Figure 9D,E showing the samples prior to and after filtration, respectively.

We further evaluated the retention of small gold nanoparticles by the macroporous separation media. Figure 10A compares the extinction spectra of the solutions in Figure 9B,C. Both samples show clear surface plasmon resonance peaks at ca. 510 nm. The peak amplitude of the filtered solution is lower than that of the original mixture because of the loss of gold nanoparticles during the filtration process. We plotted the absorbance of gold nanoparticle solutions with different concentrations at 510 nm (Figure 10B) as a calibration curve to determine the gold nanoparticle concentrations prior to and after filtration. The results demonstrated that more than 85% of gold nanoparticles were recovered after filtration. Besides hydrophobic ETPTA, a large variety of polymers ranging from highly hydrophilic PEGDA to highly hydrophobic fluorinated polymers (e.g., perfluoroether

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acrylates) can be used in DBC to create macroporous filtration membranes.

We have demonstrated above that the single-blade coating process can be utilized to create high-quality nanocomposites, colloidal crystals, and self-standing macroporous polymer membranes. Limited by the size of the commonly used doctor blades and the simple experimental setup, we have fabricated only centimeter-sized samples as proof-of-concept examples in this work. Similar DBC procedures using larger blades (up to a few meters long) and commercial DB coaters have been widely employed to create highly uniform coatings over large areas in continuous roll-to-toll processing (similar to printing newpapers).^{53–57} Because stable colloidal silica-monomer suspensions are easily available in large quantities, we believe that much larger colloidal arrays can be mass produced by using mature DBC technology. However, to reach the full potential of the roll-to-roll compatible DBC process in the large-scale fabrication of highly ordered nanocomposites, the coating speed that is limited to $\sim 5 \,\mu$ m/s by a single-blade setup (Figure 3) needs to be significantly improved. The rapid accumulation of excess colloidal suspensions that leads to a higher pressure and a thicker film reduces the achievable shear rate and the resulting crystalline quality in a fast coating system. To eliminate excess suspensions, we developed a dualblade setup as shown by the scheme in Figure 11A. The first blade removes excess colloidal suspensions and creates a uniform thin film. The second blade, which is composed of three separate subblades, then shear aligns the colloidal microspheres underneath

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them. Figure 11B shows a photograph of a sample coated at 1 mm/s by using the dual-blade setup. The sample does not show iridescent colors after passing the first blade, indicating no long-range ordering in the sample. After crossing the second blade, three iridescent stripes underneath the subblades are clearly evident whereas no diffractive colors are observed in between. This indicates that the shear stress provided by the subblades is sufficiently high to align the particles at a high coating speed. These striped colloidal arrays could find potential applications in diffractive optical devices and are available by other self-assembly technologies.⁷³ If we use a normal doctor blade instead of a blade with three subblades as the second blade in the dual-blade setup (Figure 11A), then the stripe patterns shown in Figure 11B can be prevented.

Conclusions

We have developed a scalable doctor blade coating technology for fabricating 3D highly ordered nanocomposites, colloidal crystals, and macroporous polymers. Although only centimetersized samples have been demonstrated here using our simple setup, we believe that this roll-to-roll compatible technology can be easily extended to the production of large-area coatings that have important technological applications in diffractive optics, full-color displays, and size-exclusive filtration membranes.

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