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Efficient Synthesis of Liquid Photonic Crystal by Electrically-Driven Colloid Concentration

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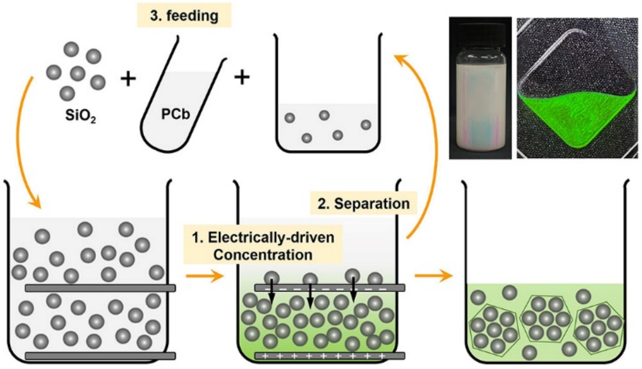

Abstract: Liquid photonic crystal (LPC) is a promising new material in the field of sensing, display, printing, and coating due to its unique fluidity, metastability, and reversibility in colloidal assembly. However, it is a big challenge to prepare LPC materials in an efficient, controllable, and eco-friendly way. In this work, an electrically-driven colloid concentration process was developed for the efficient synthesis of LPC. The key for the synthesis was that the electrophoretic process produced a locally concentrated but "agglomeration-free" colloidal solution, which spontaneously turned to LPC after being kept standing for a few minutes. The synthesis possessed good universality and reproducibility for LPCs composed of different particles and solvents. Its efficiency could be improved by tuning the particles' surface charge, the dielectric constant and viscosity of the solvent, as well as the external field conditions. More importantly, it could be developed into a large-scale and green process without chemical wastes compared to the previous synthetic methods.

Keywords: liquid photonic crystal; electrically-driven concentration; agglomeration-free; colloidal assembly; green synthesis

1. Introduction

Liquid photonic crystal (LPC) is a colloid-based photonic structure in solution. It can be considered as a mixture of the "solvent-wrapped colloidal microcrystals" and the "saturated colloidal solution" [1–4]. The former crystalline phase renders the colloidal system photonic bandgap and characteristic structural colors. While the latter amorphous phase stabilizes the ordered particle arrangement and retains the fluidity for the system at the same time. The LPC is usually converted from a highly concentrated colloidal solution, where the particles spontaneously precipitate to form colloidal crystals driven by entropy increase. On the other hand, the formed LPC only has a metastable structure so that it easily changes back to the concentrated colloidal solution under external disturbance. The aforementioned fluidity, metastability, and reversible assembly-disassembly make LPC a special colloidal system that arouses great interest in the recent research of photonic crystals.

The LPC materials are widely used in photonic sensing [5–8], optical devices [9–12], and PC synthesis [13–16] due to the above properties. First of all, the LPC is intrinsically a responsive material as its photonic properties and structural color are influenced by many physical and chemical stimuli. For example, Joo and Kang et al. [17] reported an electrically responsive LPC composed of $Fe_3O_4@SiO_2$ particles and solvent propylene carbonate (PCb). The ($Fe_3O_4@SiO_2$)/PCb LPC showed different colors at different voltages because it flexibly changed its interparticle spacing to satisfy the balance between the interparticle net repulsion and electrophoretic packing force applied to the particles. For another instance, Zhu and Ge et al. [8] developed a mesopore detection reagent based on SiO_2/(ethylene glycol) LPC. The absorption of solvent by mesopore substance changes the bandgap of LPC so that the reflection wavelength change could be used to reveal the pore volume, average pore size, and pore size distribution. Furthermore, the LPC is also a good precursor for the synthesis of solid PC and responsive PC [18–21] on different substrates because it separates the traditional PC synthesis into two steps, which addresses the conflict between synthetic efficiency and PC crystallinity. For example, Li and Shao et al. [14] utilized Polystyrene (PS)/H_2O LPC as the major component of color pastes to construct PC on textile substrates. Benefiting from the pre-assembly of particles in the LPC precursor, the shear-induced coating technique enabled efficient manufacture of large-area PC films with high crystallinity.

In the past decades, great efforts have been made to synthesize LPC in an efficient and controllable way. A traditional method is "waiting" for the spontaneous precipitation of colloidal particles from the colloidal solution [22–24]. Luck et al. [23] prepared PS/H_2O LPC with this method and demonstrated that the liquid's color originated from the ordered arrangement of particles. However, the synthetic efficiency of this method is a big concern, as several hours and even days are usually required for LPC formation. Recently, Ge et al. [4] developed an "evaporation-driven colloid concentration" process to prepare LPCs in different solvents. They well dispersed the particles in a mixing solvent and removed the volatile solvent by thermal treatment, which eventually produced the LPC in the high boiling-point solvent. The synthetic efficiency was significantly improved as the highly concentrated colloidal system led to a larger entropy increase after colloidal assembly and thereby accelerated the formation of LPC. Later, they developed a "liquid-liquid extraction" process [25] to prepare LPC, where the highly concentrated colloidal solution was achieved by extraction of solvent from the well-dispersed but diluted colloidal solution. Compared to the abundant methods to prepare solid PCs on different substrates, the synthetic route of LPC was very limited. The reported methods faced great challenges, such as the low synthetic efficiency, the requirement of high bp solvent, the consumption of large amount of extractant, etc. Therefore, there was an urgent need to develop efficient, universal, and environmentally benign method for LPC synthesis.

In this work, an electrically-driven colloid concentration process was developed for the efficient synthesis of LPC. Based on our previous research experience [4,25], the key point of the LPC synthesis was forming the highly concentrated but "agglomeration-free" colloidal system by controllable operations. The particles for colloidal assembly usually possessed high surface charges, which reminds us that the electrophoresis under an electric field was exactly the suitable process to realize particle concentration without agglomeration. In a typical synthesis, the particles were enriched near the electrode with opposite charges to form a locally concentrated solution, which was separated by the removal of supernatant and kept standing to form LPC spontaneously. In addition to the confirmation of each step in synthesis, we explored the factors influencing the synthesis efficiency, such as the particles' surface charge, the dielectric constant and viscosity of the solvent, and the electric field conditions. The universality and reproducibility of the current synthetic method were also investigated, Finally, a green synthetic process without chemical wastes was proposed to realize large-scale production of LPC materials.

2. Experimental Section

2.1. Materials

Tetraethyl orthosilicate (TEOS, 98%), aqueous ammonia ($NH_3 \cdot H_2O$, 28%), ethanol (EtOH, 99.7%), ammonium persulfate (APS, 99.5%), and isopropyl alcohol (C_3H_8O, 99.7%) were purchased from China National Pharmaceutical Group Co. Ltd. (Sinopharm) Propylene carbonate (PCb, 99%), n-Propanol (C_3H_8O, 99%), cerium(III) nitrate hexahydrate ($Ce(NO_3)_3 \cdot 6H_2O$, 99.5%), and acrylic acid (AA, 99%) were purchased from Aladdin Bio-Chem Technology Co. Ltd. Styrene (St, 99.5%) and ethylene glycol (EG, 99%) were purchased from Belling Technology Co. Ltd. Acetonitrile (C_2H_3N, 81.5%) and polyvinyl pyrrolidone (PVP, Mw = 29,000) were purchased from Sigma-Aldrich Co. Ltd. All chemicals were used as received without further treatment.

2.2. Synthesis of SiO_2 Particles

Monodisperse SiO_2 colloidal particles were prepared by a modified Stöber method. Taking the preparation of SiO_2 particles with a diameter of 180 nm as a typical example, 90 mL of TEOS was added to a mixture containing 1200 mL of EtOH, 48 mL of $NH_3 \cdot H_2O$, and 84 mL of H_2O. The above solution was continuously stirred for 9 h, during which the solution gradually changed from transparent to milky white. After the reaction, the particles were separated by centrifugation and the unreacted TEOS and $NH_3 \cdot H_2O$ were removed. After washing with ethanol 3 times, the SiO_2 particles were dispersed in EtOH for the following synthesis of liquid photonic crystals.

2.3. Synthesis of Polystyrene (PS) Particles

Monodisperse PS particles were prepared using an emulsion polymerization method. In a typical synthesis of PS particles with a diameter of 160 nm, 7 mL of styrene (St), 1 mL of acrylic acid (AA), and 100 mL of distilled water (H_2O) were mixed in a three-neck flask and stirred for 1 h under nitrogen flow. The mixture was then heated to 70 °C by heating mental. Once the temperature was stabilized, 1 mL of ammonium persulfate (APS) aqueous solution (0.1 g/mL) was added to the above mixture to initiate the polymerization. The solution was refluxed under nitrogen at 70 °C for 8 h, after which a milky white colloidal suspension was obtained. The PS particles were separated from the solution by centrifugation and washed with water 3 times. Finally, the PS particles were dispersed in water for the following synthesis of liquid photonic crystals. PS particles with different diameters could be synthesized by a similar process, except for the change of St and AA dosage or the reaction time.

2.4. Synthesis of CeO_2 Particles

Monodisperse CeO_2 particles were prepared by a high-temperature polyol process assisted with the SiO_2 nanoparticle seeds. Here, 0.087 g of arginine was added to the mixture of 5.5 mL of TEOS and 87 mL of water, which was continuously stirred under nitrogen protection at 70 °C for 24 h to obtain a transparent solution of SiO_2 nanoparticle seeds with a diameter of 20 nm. For the preparation of CeO_2 particles with a diameter of 130 nm, 24 g of $Ce(NO_3)_3 \cdot 6H_2O$, 12.5 g of PVP, 750 μL of the SiO_2 seed solution, and 100 mL of EG were mixed in a three-neck flask. The mixture was stirred under nitrogen and heated to react at 155 °C for 1 h, during which the transparent solution gradually transformed into a yellow colloidal suspension. After the reaction, the mixture was cooled down to room temperature, and the CeO_2 particles were separated by centrifugation and washed with EtOH three times. Finally, the CeO_2 particles were dispersed in EtOH for the following synthesis of liquid photonic crystals. Its diameter could be controlled by adjusting the dosage of $Ce(NO_3)_3 \cdot 6H_2O$ and PVP in synthesis.

2.5. Construction of the Electrophoretic Cell for Particle Concentration

In the prototype experiment, we used a plastic cuvette equipped with two parallel copper electrodes as the electrophoretic cell for particle concentration. The plastic cuvette was a commonly used consumable with size of 1 cm × 1 cm × 4.5 cm. Two Cu plates were horizontally inserted into the plastic cuvette with interspacing of 0.5 cm or 1 cm. The parallel Cu electrodes were fixed on the cuvette by epoxy adhesives, which also sealed the cuvette to avoid leakage of the solution.

2.6. Preparation of SiO_2/EtOH LPC by Electric Field-Assisted Concentration

In a typical process, a diluted SiO_2/EtOH solution with a particle volume fraction of 5% was first prepared by sufficient sonication of particles in solution. The initial particle volume fraction in a specific solvent should be low enough to ensure the generation of agglomeration-free colloidal suspension. Then, 1 mL of the SiO_2/EtOH solution was added to the cuvette with an electrode interspacing of 0.5 cm. After the Cu electrodes were connected to the direct current (DC) power source, a voltage of 8 V was applied to drive the SiO_2 particles moving toward the bottom electrode with a positive charge. After the electrophoresis for several minutes, a concentration gradient formed in the solution, and most of the particles were concentrated at the bottom between the electrodes. Finally, half of the solution above the upper electrode was carefully removed by pipette, leaving behind a concentrated but “agglomeration-free” colloidal solution to produce the LPC spontaneously.

2.7. Large-Scale Synthesis of SiO_2/PCb LPC by Green Approaches

The green synthesis of LPC was generally composed of the electrically-driven particle concentration, the separation of the supernatant colloidal solution, and the feeding of dried colloids and solvents. The first two steps were similar to the procedures above. In a typical process, 1 mL of SiO_2/PCb solution with particle volume fraction (f_{SiO2}) of 8.69% (m =177.3 mg) was used as the initial colloidal dispersion. Firstly, the SiO_2 particles in PCb were concentrated around the electrode with a positive charge by the application of an electric field. Secondly, liquid-liquid separation was used to obtain 0.5 mL of LPC and 0.5 mL of supernatant colloidal solution. The mass of SiO_2 particles in the LPC and the supernatant was measured to be 158 mg and 19.3 mg. Thirdly, 0.5 mL of fresh PCb and 158 mg of dry SiO_2 particles were added to the supernatant solution to form the diluted SiO_2/PCb solution for next-round preparation. Through multiple cycles of electrically-driven concentration, separation, and feeding, the f_{SiO2} of the LPC and the supernatant colloidal solution gradually achieved stable values, which were 15.49% and 1.89%, respectively.

2.8. Measurement of the Volume Fraction of Colloidal Particles in Solution

For a typical measurement of the volume fraction of SiO_2 particles (f_{SiO2}) in solution, 200 μL of the colloidal solution was taken for centrifugation at 11,000 rpm for 5 min, after which the supernatant solution was carefully removed. Then, the SiO_2 particles were placed in an oven at 120 °C and dried for 4 h to completely remove the residual solvent. The mass of the SiO_2 particles was accurately measured to determine their volume, which was finally used to calculate the particle volume fraction in the colloidal solution.

Characterizations: The reflection spectra were recorded by an Ocean Optics Maya 2000 Pro spectrometer coupled to a six-around-one reflection probe, where both the incident and reflective angle were fixed at 0°. The morphology and the size of the colloidal particles were characterized by the Hitachi S4800 scanning electron microscope (SEM). The optical microscopy images were collected by an Olympus BXFM reflection-type microscope operated in dark-field mode. The Zeta potential of colloidal particles in the solution was measured by Malvern Zetasizer Nano ZS90 at room temperature.

3. Results and Discussion

In a typical synthesis, the SiO_2/EtOH liquid photonic crystal (LPC) was prepared by an “agglomeration-free” concentration under an electric field, the removal of the supernatant colloidal solution, and a spontaneous colloidal assembly in the concentrated solution (Figure 1a). In the step of concentration, a diluted SiO_2/EtOH solution with a typical particle volume fraction (f_{SiO2}) of 5% was first loaded to the cuvette equipped with horizontally parallel copper electrode. Here, one electrode was placed at the bottom of the cuvette and the other was fixed at half height of the colloidal solution. According to the simulation of potential distribution, the colloid particles in the upper solution were majorly in Brownian motion and those in the bottom solution would migrate orientationally towards one electrode (Figure 1b). Once a voltage was applied, the negatively charged SiO_2 particles moved towards the bottom electrode with opposite charges, which produced a concentrated colloidal solution between two electrodes in a few minutes. In the step of separation, the upper solution containing very few particles was removed in the presence of the electric field, and the bottom solution was left standing to form LPCs with structural colors. Besides the photos for each step, the effective concentration of particles under the electric field could also be confirmed by the change of transmission spectra, where the transmittance of the concentrated solution was lower than that of the initial solution, and the transmittance of the supernatant was higher than the initial (Figure 1c,d).

It should be noted that the key point for the synthesis was the “agglomeration-free” concentration under an electric field. It is extremely difficult to form a highly concentrated colloidal solution without any agglomerations by directly dispersing a large amount of colloidal powder in the solvent. Therefore, the synthesis started from a diluted colloidal solution where the particles could be well dispersed at that low concentration. Then, the electrophoretic conditions were controlled to effectively but gently enrich the particles in the liquid environment. It led to the formation of a concentrated but “agglomeration-free” colloidal system, which was exactly the precondition for the LPCs.

In some cases, multistep concentration under an electric field helped produce LPCs with larger f_{SiO2} and higher crystallinity. Here, we investigated the regulations in the multistep concentration of SiO_2/EtOH through the change in f_{SiO2}, the concentration efficiency (f_n/f_{n-1}), and the reflection spectra (Figure 1e–g). As the concentration time increased from 1 to 3, the SiO_2 particles were gradually enriched in ethanol and the f_{SiO2} increased from the original 5.8% to 12%, 22%, and 35%, respectively (Table S1). Meanwhile, the concentration efficiency defined as the ratio of f_{SiO2} after and before the concentration decreased from 2.1 to 1.5 probably because the increase in viscosity inhibited the movement of colloidal particles under the same electric field. Along with the three-step synthesis, the reflection wavelength of the as-made LPC blue shifted from 813 nm to 745 nm and 672 nm because the increase of f_{SiO2} significantly decreased the lattice spacing of colloidal crystals. At the same time, the reflection intensity became stronger as the increase of f_{SiO2} also favored the assembly of particles into a more ordered structure. Based on the above experiments, the electrically-driven multistep concentration could be used to prepare LPCs with different bandgaps and structural colors. It was also useful to prepare some LPCs that required a very high f_{SiO2} to achieve the spontaneous colloidal assembly.

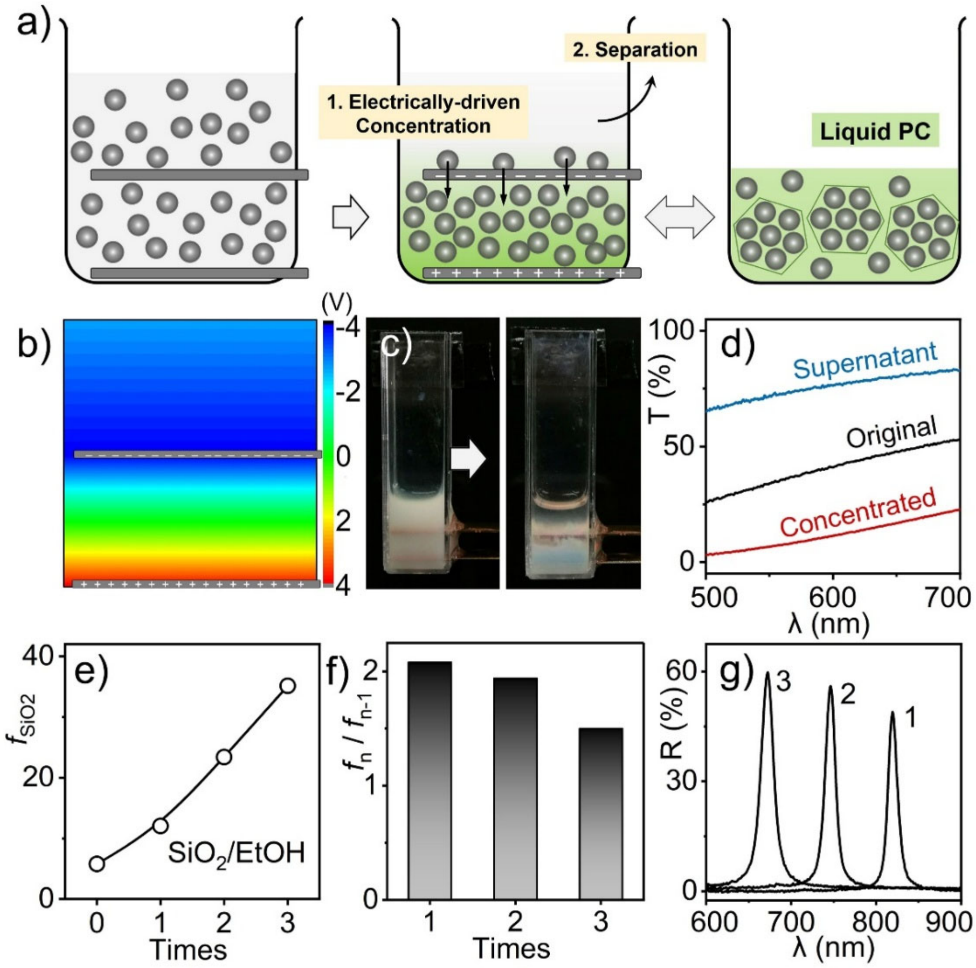

Figure 1. Synthesis of LPC by electrically-driven colloid concentration. (**a**) Scheme for the synthesis of LPC through electrically-driven concentration followed by liquid-liquid separation; (**b**) the simulated distribution of the potential in the solution; (**c**) the photo of the SiO_2/EtOH colloidal solution before and after concentration; (**d**) the transmission spectra of the originally diluted colloidal solution, the concentrated colloidal solution, and the supernatant; the evolution of (**e**) the particle volume fraction (f_{SiO2}), (**f**) the concentration factor (f_n/f_{n+1}), and (**g**) the reflection spectra of the generated LPC after 3 times of concentration.

The highly concentrated SiO_2/EtOH colloidal solution prepared by electrically-driven concentration exhibited typical characteristics of the liquid photonic crystals. First of all, the SiO_2/EtOH LPC was a fluid with two phases coexisted, where the structural color originated from the crystalline phase (Figure 2a–f). As proved by the previous study, the LPC was composed of a crystalline and an amorphous phase, which referred to the solvent-wrapped colloidal crystals and the saturated colloidal dispersion, respectively. These two phases could be directly recognized as the colored and the colorless domains in the microscope image. They could also be confirmed by the difference in their microscale reflection spectra, where the reflection intensity of the crystalline phase was higher. When the LPC was carefully dried in the air, these two phases were retained so one could observe the ordered and disordered particle arrangement in their SEM images. For the second feature, the LPC was a metastable structure, which allowed reversible colloidal assembly and disassembly (Figure 2g–i). In the absence of external disturbance, the SiO_2/EtOH colloidal solution spontaneously formed the SiO_2/EtOH LPC in several seconds. While the LPC quickly turned back to the colloidal solution if the LPC was mechanically disturbed. When these two processes occurred alternatively, the reflection intensity rose and fell periodically, which indicated that the assembly and disassembly were fully reversible.

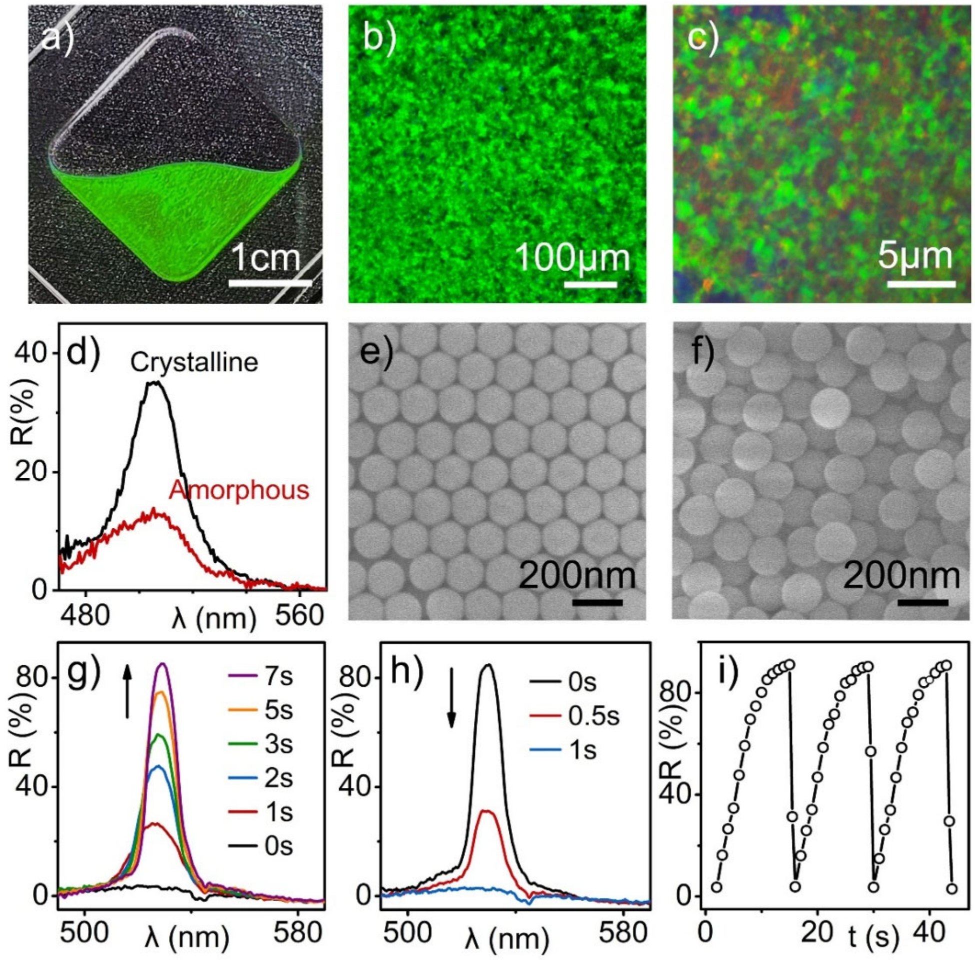

Figure 2. Characteristics of the SiO₂/EtOH LPC. (**a**–**c**) Digital photos and optical microscope images of the SiO₂/EtOH LPC; (**d**–**f**) microscopic reflection spectra of the crystalline and amorphous region of the LPC and the SEM images of the corresponding region after careful drying; (**g**–**i**) reversible colloidal assembly and disassembly proved by the periodic change of the reflection intensities.

Since the LPC synthesis was achieved by the particle electrophoresis and the electrically-driven colloid concentration, the properties of the colloids and solvent as well as the external field conditions became the key factors to ensure the formation of LPC and improve the synthetic efficiency. For the LPC formation, the solvents were usually polar solvents and the particles had ionizable groups so that the particles could have adequate strong surface charge to realize the colloidal assembly through electrostatic repulsion. Furthermore, the external voltage should be as low as possible to avoid electrochemical reactions during the synthesis. For the synthetic efficiency, one could find solutions in the well-known electrophoresis formula (Equation (1)). In this equation, the particle migration speed (v) is proportional to the particles' surface potential (ζ), the solvent's dielectric constant (ε), and the applied voltage (E). Meanwhile, the speed is inversely proportional to the distance between two electrodes (d) and the solvent's viscosity (η). Therefore, any adjustment that favored the increase of υ would improve the synthetic efficiency (Figure 3a). In the following discussion, we investigated the strategies to improve the efficiency in the aspects of colloidal particles, the solvent medium, and the electric field conditions.

$$v = (\zeta\cdot\varepsilon\cdot E)/(k\cdot\pi\cdot d\cdot\eta) \quad (1)$$

Firstly, the particle with a high surface charge was favorable to the efficiency of LPC synthesis. Here, we dispersed SiO_2, polystyrene (PS), or CeO_2 particles in EtOH to form a diluted colloidal solution, which was used to prepare LPC via electrically-driven concentration under the same conditions. The particle volume fraction (f_p) was continuously monitored in three concentrations and the total concentration factors (TCF) were calculated to indicate the synthetic efficiency. The experiment suggested that the f_p increased along with the electrically-driven concentration in all cases. The TCF for SiO_2/EtOH, PS/EtOH, and CeO_2/EtOH solution were then calculated to be 8.7, 6.3, and 3.0, respectively (Figure 3b,c). The decrease in TCF was believed to be tightly related to the surface charge of the particles, where the ζ of SiO_2, PS, and CeO_2 particles were measured to be −40 mV, −37 mV, and

+30 mV, respectively. Among them, SiO_2 particles possessed the highest surface charges, which led to the fastest migration speed, facilitated the concentration of colloids under the electric field, and eventually improved the synthetic efficiency.

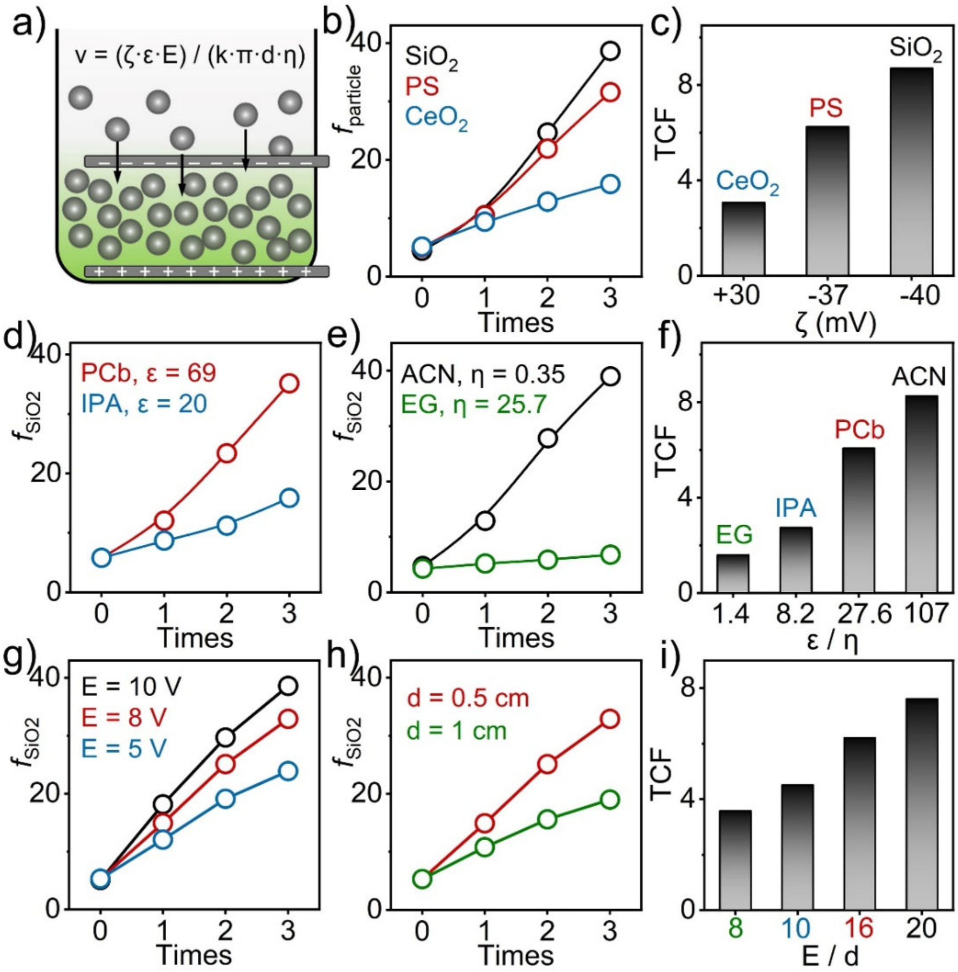

Figure 3. Factors influencing the synthetic efficiency. (**a**) Schematic diagram showing that the efficiency of LPC synthesis was determined by the particle migration speed; (**b**,**c**) evolution of the particle volume fraction in 3 times of concentration and the total concentration factor (TCF) for the ethanol solution of CeO_2, PS, and SiO_2 particles with different zeta potentials (ζ); (**d**–**f**) evolution of the f_{SiO2} for four colloidal solutions composed of different solvents and the independence of TCF upon the ratio of dielectric constant and viscosity (ε/η); (**g**–**i**) evolution of the f_{SiO2} under different electric field conditions and the independence of TCF upon the ratio of the external voltage and the electrode spacing (E/d).

Secondly, the solvent with a high dielectric constant and low viscosity also favored the efficiency of LPC synthesis. Here, we designed SiO_2/propylene carbonate (PCb) and SiO_2/isopropyl alcohol (IPA) diluted solutions for LPC synthesis under the same condition, where PCb and IPA possessed close viscosities (η = 2.50, 2.43) but different dielectric constants (ε = 69.0, 19.9) (Figure 3d, Table S2). After three rounds of electrically-driven concentration, the f_{SiO2} in PCb (35.1%) was much higher than that in IPA (15.9%), which suggested that a large dielectric constant accelerated the migration of colloidal particles and then improved the concentration efficiency. Similarly, we designed SiO_2/acetonitrile (ACN) and SiO_2/ethylene glycol (EG) solutions for LPC synthesis, where ACN and EG had close dielectric constants (ε = 37.5, 37.0) but different viscosities (η = 0.35, 25.7) (Figure 3e). After three continuous concentrations, the f_{SiO2} in ACN (39.0%) was much higher than that in EG (6.8%), which suggested that a low viscosity decreased the resistance of particle migration in solvent and thereby improved the concentration efficiency. Since every solvent had different ε and η, one could combine their influence with the ε/η ratio according to Equation (1) (Figure 3f). When the 4 SiO_2 colloidal systems were compared in the concentration efficiency, the TCF exactly increased with the increasing of the ε/η ratios, which again demonstrated the high dielectric constant and low viscosity favored the synthetic efficiency.

Thirdly, the efficiency of LPC synthesis could be improved by the application of a strong electric field. Here, we took the SiO_2/PCb solution for electrically-driven concentration and investigated the influence of the external voltage (E) and the electrode spacing (d) (Figure 3g,h). As the applied voltage increased from 5 V to 10 V, the f_{SiO2} after three rounds of concentration increased from 26% to 35%. In parallel control experiments, the f_{SiO2} after concentration increased from 24% to 28% when the electrode spacing decreased from 1 cm to 0.5 cm. When the above tests were arranged in the order of increasing E/d ratio, one could find that their TCF increased with the strength of the electric field (Figure 3i). It confirmed that a strong electric field was favorable to the fast migration of particles and the higher concentration efficiency. It should be noted that a voltage higher than 10 V was not acceptable as it caused particle agglomerations around the electrode. An electrode spacing smaller than 5 mm was not preferred either because it brought challenges to the liquid-liquid separation and decreased the production yield of the LPCs. In a word, the electrically-driven concentration method was suitable for preparing LPCs composed of highly charged particles and solvents with large dielectric constant and low viscosity. A voltage of 8 V, an electrode spacing of 0.5 cm, and a 10-min concentration could be the optimized conditions for most synthesis in the current work.

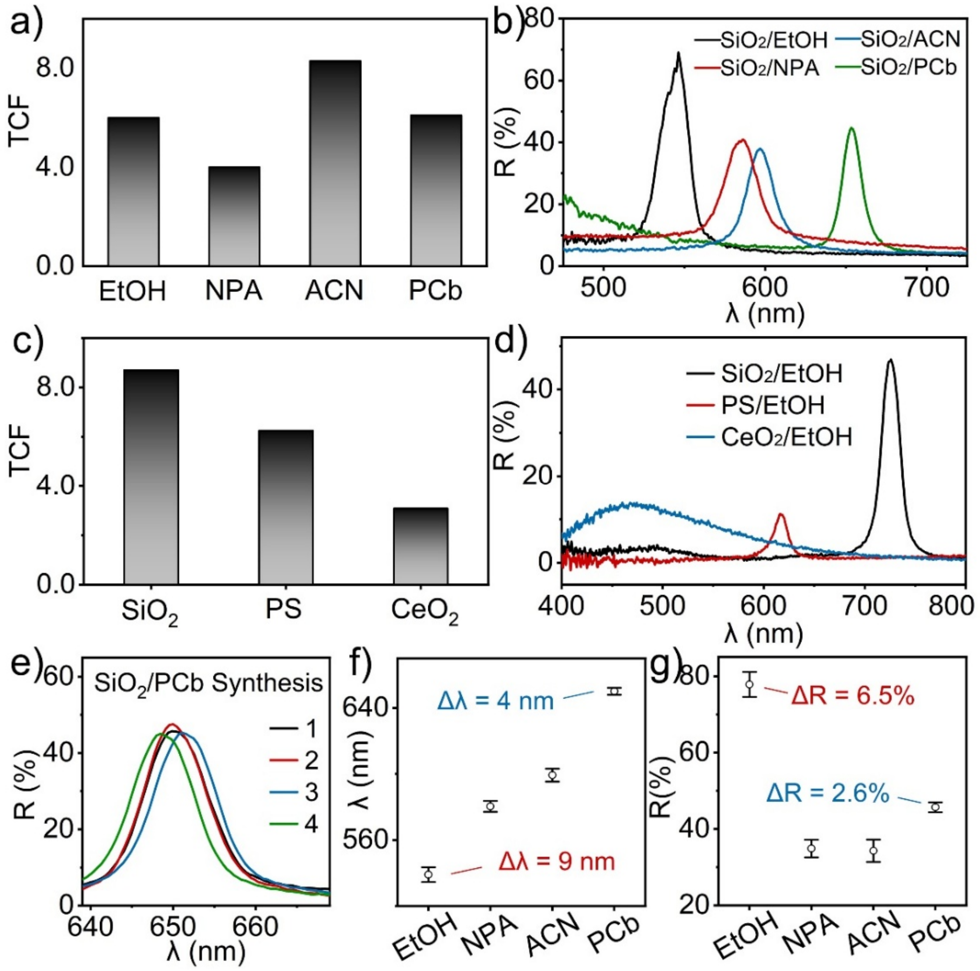

Figure 4. Universality and reproducibility of the synthetic method. (**a**–**d**) TCF values when synthesizing LPCs composed of different colloidal particles or solvents and the reflection spectra of the generated LPCs; (**e**) the reflection spectra of four SiO_2/PCb LPC samples prepared in different batches; (**f**,**g**) the deviation of λ and R for the LPCs prepared in different batches.

The electrically-driven colloid concentration was a convenient and universal method for the synthesis of LPCs composed of different particles and solvents. For example, this method was feasible for the synthesis of LPCs composed of SiO_2 particles and various solvents, including ethanol (EtOH), n-propanol (NPA), acetonitrile (ACN), and propylene carbonate (PCb) (Figure 4a,b). Starting with the same initial f_{SiO2} around 5.5%, the SiO_2 particles in all systems could be effectively concentrated by 3 cycles of electrophoresis, which could be proved by their TCFs around 4 to 5. The agglomeration-free concentration led to the formation of SiO_2/EtOH, SiO_2/NPA, SiO_2/ACN, and SiO_2/PCb LPCs, which was confirmed by the strong reflection peaks at different wavelengths due to the different particle fraction and different refractive indices. Furthermore, this method was also applicable to

LPCs composed of ethanol and different colloids, including SiO_2, PS, and CeO_2 (Figure 4c,d). The formation of SiO_2/EtOH, PS/EtOH, and CeO_2/EtOH LPCs was supported by their reflection spectra and TCF values after 3 cycles of electrically-driven concentration. The low crystallinity of the CeO_2/EtOH LPC was related to the relatively low surface charge of CeO_2 particles and thereby the low concentration efficiency under the electric field. It could be improved by enhancing the field strength or increasing the concentration times.

In addition to the universality, the current synthetic method also possessed satisfactory reproducibility in parallel productions (Figure 4e–g). Here, the syntheses of SiO_2/EtOH, SiO_2/NPA, SiO_2/ACN, and SiO_2/PCb LPCs were performed 4 times on different days, and the corresponding reflection spectra were recorded and compared to examine the reproducibility. The LPCs prepared in parallel batches had very close compositions and bandgap structures, which could be confirmed by the 4 reflection peaks with very close wavelengths and intensities. A little fluctuation in the reflection signal might originate from the evaporation of solvent during the synthesis, which slightly changed the particle volume fraction and eventually altered the lattice constant and the crystallinity of the generated LPCs. In our experiments, the synthesis of SiO_2/PCb LPC showed a smaller deviation than the other syntheses, which could be explained by its high boiling point and low volatility. Nevertheless, the reproducibility was satisfactory and it might be improved when the synthesis scale was further amplified.

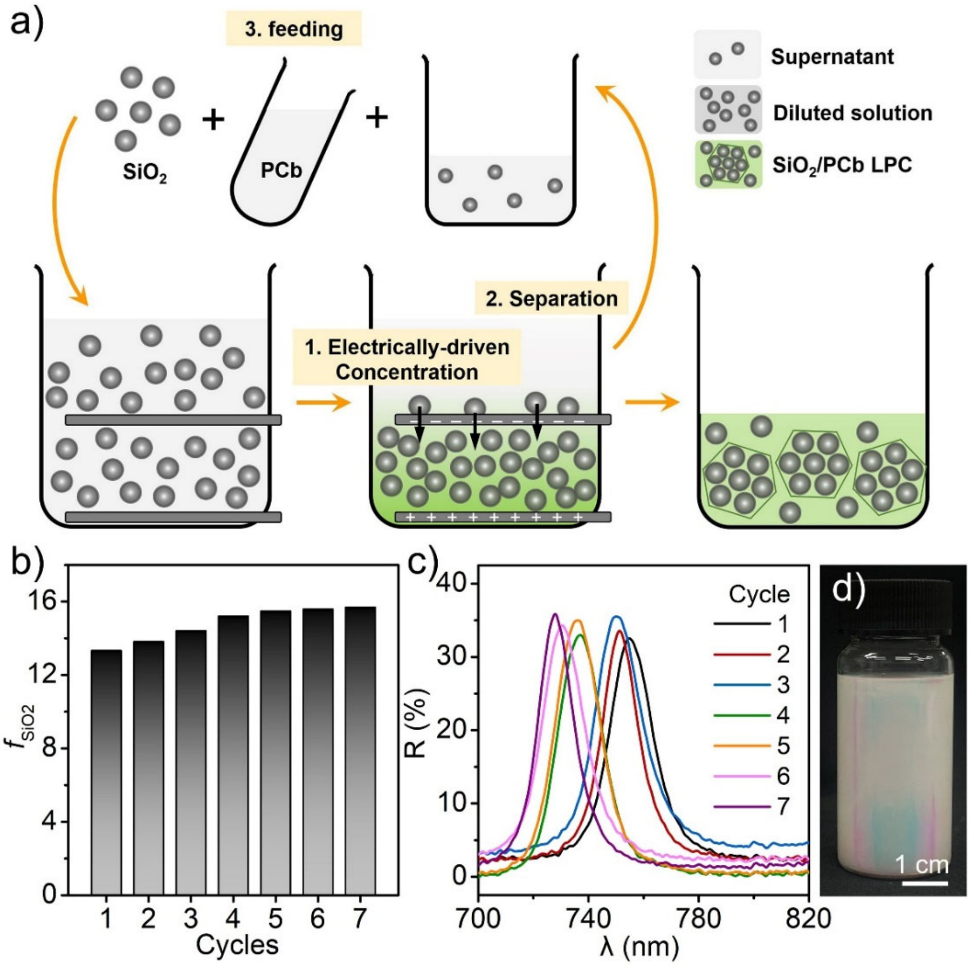

Figure 5. Large-scale and green synthesis of LPC. (**a**) Green synthetic route based on the electrically-driven concentration, liquid-liquid separation, and the feeding of colloids and solvent; (**b**) evolution of the f_{SiO2} in 7 times of closed-loop synthesis and (**c**) the reflection spectra of the corresponding LPC prepared by this method; (**d**) the photo of the concentrated SiO_2/PCb colloidal solution, which transforms into LPCs later.

Through the recycling of the supernatant colloidal solution from separation, the current method could be developed into a large-scale synthetic process for green production of LPC materials (Figure 5a). Taking the synthesis of SiO_2/PCb LPC as an example, the 1st round LPC product was achieved by an electrically-driven colloid concentration followed by a liquid-liquid separation of the supernatant colloidal solution. Since the supernatant solution contained a few SiO_2 particles ($f_{SiO2} = 1.89\%$) and half of the PCb solvent, it could be mixed with the supplied PCb and SiO_2 powders to form a new "diluted colloidal solution" for the next round electrically-driven concentration. With the joining of the feeding step, the whole synthesis became a closed loop, which continuously produced LPC materials on a large scale without wasting the colloids and solvent. In the practical experiment, the f_{SiO2} of the LPCs produced in each cycle gradually increased to a stable value ($f_{\mathrm{SiO2}} = 15.49\%$), and the reflection of the LPC blue shifted to a stable wavelength accordingly, both of which confirmed the large-scale production of LPC material with a stable composition and optical property (Figure 5b–d). Unlike the traditional synthesis of LPCs based on evaporation-driven colloid concentration and liquid-liquid extraction, the current synthesis fully utilizes the source material and realizes zero emission in production.

4. Conclusions

In summary, an electrically-driven colloid concentration process was developed for the efficient synthesis of liquid photonic crystals (LPC). Colloidal particles first migrated towards the electrode with opposite charges and formed a locally concentrated but “agglomeration-free” solution. After removing the supernatant by liquid-liquid separation, the concentrated colloidal solution spontaneously formed LPC in the absence of external disturbance. Multiple concentrations could be performed to produce LPCs with larger f_{SiO2} and higher crystallinity. The as-prepared colloidal system exhibited typical characteristics of LPC including two-phase coexistence, structural color, metastable structure, and reversible colloidal assembly and disassembly. The “electrically-driven concentration” method was suitable for preparing LPCs composed of highly charged particles and solvents with large dielectric constant and low viscosity, as these conditions favored fast particle migration under the electric field. The voltage was set around 8 V to maintain the high efficiency and avoid electrochemical reactions. This method exhibited good universality and reproducibility for the synthesis of LPCs composed of different particles and solvents. More importantly, it could be developed into a large-scale and green synthetic process without chemical wastes through the recycling of the supernatant colloidal solution, which guaranteed the supply of responsive LPC material for related applications.

Supplementary Materials: The following supporting information can be downloaded at: https://www.sciltp.com/journals/mi/2025/1/699/s1. Table S1: Change of particle volume fraction by electrically-driven colloid concentration; Table S2: Physical properties of the used solvents.

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