

# Solvent Wrapped Metastable Colloidal Crystals: Highly Mutable Colloidal Assemblies Sensitive to Weak External Disturbance

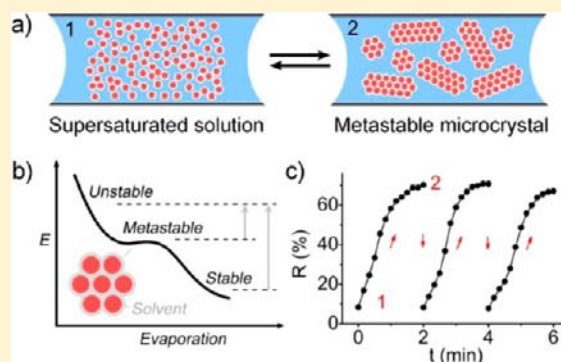
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**S** Supporting Information

**ABSTRACT:** Solvent wrapped “metastable” crystalline colloidal arrays (CCAs) have been prepared by supersaturation induced precipitation and self-assembly of monodisperse particles in polar/nonpolar organic solvents. These metastable CCAs possess ordered structures but with less stability comparing with traditionally fixed colloidal crystal systems. They are stabilized by the balance between long-range attraction and electrostatic repulsion of neighboring like-charged particles. Monitoring the reflection intensity during evaporation suggests that these crystals can exist for several hours at 90 °C and even longer at room temperature. Based on the evolution of particle volume fraction in whole suspension ( $\phi_{\text{SiO}_2}$ ), crystal phase ( $\phi_{\text{crystal}}$ ), and liquid phase ( $\phi_{\text{liquid}}$ ), the formation of metastable CCAs can be understood as a microscopic phase separation process, where the homogeneous dispersion will separate into a “crystal phase” with orderly stacked particles and a “liquid phase” with randomly dispersed particles. Further calculation of the volume fraction of crystal phase ( $V_{\text{crystal}}/V_{\text{total}}$ ) and the ratio of particles in crystal phase ( $f_{\text{crystal}}$ ) shows that with the increase of designed  $\Phi_{\text{SiO}_2}$ , more particles precipitate to form colloidal crystals with larger sizes but the lattice spacing of the microcrystals remains constant. Unlike fixed or traditional responsive CCAs, these metastable CCAs can reversibly assemble and disassemble with great ease, because little energy is involved or required in this transformation. Therefore, they can sense weak external disturbances, including subtle motion and slight friction or shearing forces.



## 1. INTRODUCTION

Crystalline colloidal arrays (CCAs) and their derived responsive materials have attracted great interest in recent years due to their applications in sensing,<sup>1–5</sup> biomolecule detection,<sup>6–8</sup> displays,<sup>9,10</sup> printing,<sup>11–13</sup> security devices,<sup>14,15</sup> optical enhancement,<sup>16,17</sup> and solar cells.<sup>18,19</sup> Intrinsically, most evaporation induced colloidal assembly can be regarded as a concentration process, in which the volume fraction of building blocks gradually increases from a low value (usually 3–5%) to a maximum (74%). In this process, the particles, which are initially well dispersed in solution, will assemble into a close-packed CCA as the solvent fully evaporates. In the final stage of assembly, one can imagine that the particles will precipitate out of their concentrated solution to form colloidal microcrystals infiltrated with solvent, which turn into a solvent-free CCA soon afterward.

According to the definition of metastability, a solvent wrapped colloidal crystal is in a metastable state, because it exists for a finite lifetime in some conditions but possesses less stability than dried or fixed stacks of particles. Its internal energy is certainly higher than the energy of the dried CCA (stable state), but slightly lower than that of a supersaturated suspension of particles in Brownian motion (unstable state).

Therefore, such a metastable CCA is born with greater flexibility toward changes in its crystal structure compared with a fixed CCA, because much less energy is required to raise it to the unstable state. Based on this characteristic, it should have intrinsic advantages such as a fast response and good sensitivity to very weak external stimuli. However, it is difficult to prepare, separate, and utilize a metastable CCA, because it quickly transforms to the stable structure in most evaporation induced assembly processes.

In this work, solvent wrapped “metastable” colloidal crystals were prepared by precipitation and self-assembly of colloidal particles in supersaturated solutions. The synthesis is a universal and straightforward process, and the suspension of colloidal crystals is primarily composed of monodisperse particles and a high boiling point solvent. Since the “metastable” CCAs are less stable than solid crystals with fixed structures, very little energy is required to change their morphologies and optical signals. Therefore, they can disassemble instantly after a weak disturbance and assemble again after settling for a few minutes. When the colloidal

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crystals were sandwiched between two glass slides, they were found to be extremely sensitive to slow movements of the glass slides and weak friction or shearing forces on the scale of  $10^{-6}$  to  $10^{-8}$  N.

Compared with the reported “metastable” CCAs over the past 40 years,<sup>20–24</sup> the current work represents significant improvements in synthesis, physical insights, and applications. Previous syntheses were mostly based on the direct assembly of “de-ionized” polystyrene particles in water or “sterically” stabilized polymer particles in organic solvents, which usually lasted for hours to days and needed complicated pretreatment. This work utilizes the evaporation of a volatile *good solvent*, in which SiO<sub>2</sub> particles can be easily dispersed, in a higher boiling point *target solvent* to initiate supersaturation of particles and assemble them into colloidal crystals within several minutes. Our process is more efficient and controllable than previous works, and it is also universal for different solvent systems. In terms of physical insights, previous works generally established phase diagrams based on “macroscopic” phase separations, revealing the influence of particle volume fraction, salt concentration, or external electric field upon the crystallization and crystal structures. Our work reported here proves that even in a seemingly homogeneous CCA suspension, a “microscopic” phase separation always exists, thus revealing a clearer and more accurate physical image. More importantly, we propose the concept of “metastable colloidal crystal” to define the solvent wrapped non-close-packed CCA and demonstrate its unique applications for fast and effective sensing of weak mechanical forces, making it an important component in the family of polymeric responsive colloidal crystals.

## 2. EXPERIMENTAL SECTION

**2.1. Materials.** Tetraethylorthosilicate (TEOS, 98%), aqueous ammonia (28%), *N,N*-dimethylformamide (DMF, 99.5%), and dimethyl sulfoxide (DMSO, 99%) were purchased from Sinopharm Chemical Reagent Co. Ltd. Aniline (99.9%), anisole (99%), and amyl butyrate (99%) were purchased from Aladdin Co. Ltd. Oleylamine (OAm, 96%), ethylene glycol (EG, 99%), and ethanol (99.9%) were purchased from J&K Co. Ltd. 1,2-Dichlorobenzene (DCB, 98.0%) was purchased from TCI Co. Ltd. All chemicals were used directly as received without further purification.

**2.2. Preparation of Metastable CCAs in Polar Solvents.** Monodisperse silica particles were first synthesized using the Stöber method. The particles (0.03, 0.04, or 0.05 cm<sup>3</sup>) were well dispersed in a good solvent (ethanol or acetone, 1 mL) by sonication and then mixed with the target solvent (0.07, 0.06, or 0.05 mL), which may vary from EG to DMF or DMSO. A small amount of carbon powder (0.05%) can be introduced in this stage. The volumes of the silica particles and the target solvent should be calculated before mixing so that a designed volume fraction of colloidal particles ( $\Phi_{\text{SiO}_2} = 0.3–0.5$ ) can be achieved after the evaporation of good solvent. The mixture was then transferred to an oven at 90 °C. After 2 h of solvent evaporation, about 0.1 mL of liquid was cooled to room temperature. The liquid suspension was sandwiched between two glass slides, and metastable colloidal crystals formed within several minutes.

**2.3. Metastable CCAs in Nonpolar Solvents.** The synthesis of metastable CCAs in aniline, anisole, DCB, and amyl butyrate was almost the same as that in polar solvents, except that oleylamine (10  $\mu\text{L}$ ) was added to the ethanol solution of SiO<sub>2</sub> particles before they were mixed with the nonpolar solvents.

**2.4. Determination of Particle Volume Fraction.** Generally, the supersaturated solution of particles after evaporation is composed of three components: the particles, the target solvent (EG, DMF, etc.), and the residue of the good solvent (ethanol or acetone). For a typical sample, their respective volumes are 30, 70, and 15.4  $\mu\text{L}$ . First, the particle volume is precisely controlled by mixing a specific amount of

SiO<sub>2</sub>/ethanol solution with EG before evaporation. To determine the volume of SiO<sub>2</sub> in the ethanol solution, the SiO<sub>2</sub> particles were dispersed in a defined amount of ethanol. After adequate sonication, 1 mL of the above suspension was transferred to a centrifuge tube. The SiO<sub>2</sub> particles were separated by centrifugation, dried in an oven, and weighed by electronic balance, so that the accurate mass and then volume concentration of SiO<sub>2</sub> particles in ethanol could be obtained. Based on this parameter, one can easily introduce 30  $\mu\text{L}$  of SiO<sub>2</sub> particles into the precursor. Second, the volume of the target solvent, EG, could be controlled when it was added to the SiO<sub>2</sub>/ethanol solution. Third, the amount of residual ethanol could be determined by the mass increment of the final solution compared with the theoretical masses of the SiO<sub>2</sub> particles and EG, because the latter two were not lost during evaporation. The volume of ethanol was then calculated using its mass and density. Knowing the volumes of all three components, one can calculate the actual particle volume fraction ( $\phi_{\text{SiO}_2}$ ) in solution, assuming no volume change occurs during the mixing process.

**2.5. Characterization.** The particle size was determined using a JEOL JEM-2100 transmission electron microscope. The optical microscope images were taken on an Olympus BXFM reflection-type microscope operated in dark-field mode. The reflection spectra were measured using an Ocean Optics Maya 2000 Pro spectrometer coupled to a six-around-one reflection/back scattering probe, where both the incident and reflective angles were fixed at 0°.

## 3. RESULTS AND DISCUSSION

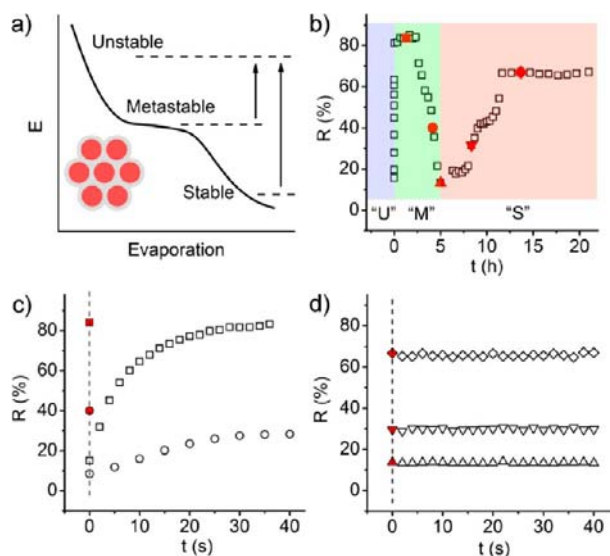
**3.1. Characteristics of Metastable CCAs.** The metastable CCAs were prepared by self-assembly of silica particles in their supersaturated solutions. Typically, monodisperse particles were first dispersed in a *good solvent* with a low boiling point, such as ethanol, methanol, or acetone. The resulting dispersion was then mixed with one high bp *target solvent* listed in Table 1

**Table 1. Boiling Points, Viscosities, Dielectric Constants, and Refractive Indices of the Solvents Used**

	bp (°C)	$\eta$ (mPa·s)	$\epsilon$	$n$
DMF	153	0.82	36.7	1.43
DMSO	189	1.99	45.0	1.48
EG	197	19.9	38.7	1.43
DCB	180	1.32	9.82	1.55
aniline	184	4.5	7.0	1.59
amyl butyrate	186	1.23	3.9	1.41
anisole	155	7.11	4.3	1.52

to form a homogeneous solution at room temperature. There are many feasible combinations utilizing any pairing of one good solvent and one target solvent (Supporting Information, sections 1 and 2) The amount of each component was precisely tuned to achieve the desired particle volume fraction ( $\Phi_{\text{SiO}_2} = 0.3–0.5$ ) in the *target solvent*. After the good solvent was evaporated in an oven, the liquid suspension was cooled to room temperature, and metastable CCAs would spontaneously precipitate out of the target solvent after 10 min. These suspended colloidal microcrystals strongly diffract visible light and render the solution brilliant and monochromatic colors.

The metastability of the reported colloidal microcrystal originates from its specific composition and structure. Upon comparison of the particle diameter with the center-to-center distance of neighboring particles in the metastable CCA, which will be calculated from  $\lambda$  later in this paper, it is clear that solvent fills the gaps between particles and prevents them from contacting one another (inset of Figure 1a). Therefore, this structure can be regarded as a “solvent wrapped” CCA, which is



**Figure 1.** (a) Hypothesized evolution of internal energy of particle suspension during evaporation. (b) Evolution of reflection intensity ( $R$ ) when a supersaturated solution of particles is placed at  $90\text{ }^{\circ}\text{C}$  for 21 h. The status of colloidal crystals can be classified into “unstable” (blue zone), “metastable” (green zone), or “stable” (red zone) states, according to evolution of  $R$  in panel b and the evaporation. (c, d) The following recovery process after the colloidal crystals are disturbed.

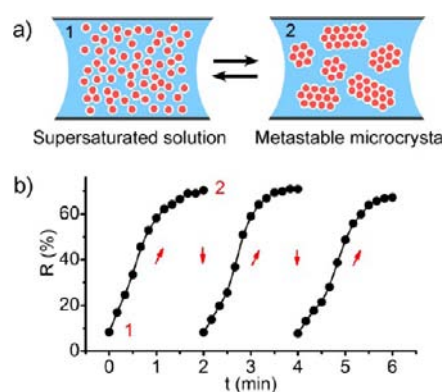
different from CCAs formed by the stacking of dry particles or CCAs fixed in a polymer matrix. This kind of colloidal crystal is termed a “metastable” CCA because it is less stable than the traditional fixed CCA but it does maintain an ordered crystal structure under certain conditions.

Generally, the solvent wrapped metastable colloidal crystals only exist momentarily in traditional evaporation induced colloidal assembly. The value of the current synthesis is that it provides an effective way to create a “metastable plateau” in a relatively long period by replacing the volatile solvent with a nonvolatile one. In order to understand how this plateau forms, one has to define the unstable, metastable, and stable states of colloidal particles first. Here, the “unstable” state corresponds to the supersaturated solution of particles, which will spontaneously and continuously precipitate to form more or larger colloidal crystals. The “metastable” state summarizes the characteristics of the precipitated solvent wrapped colloidal crystals, which possess an ordered but very mutable crystal structure. The “stable” state describes the fixed colloidal crystals after most or all solvent is evaporated, where the crystal structure will not change any more.

The evolution of reflection intensity ( $R$ ) in an accelerated evaporation process confirms the hypothesized energy change of colloidal crystals and proves that a metastable plateau does exist in this process (Figure 1). Because the ordered colloidal crystal has structure-related reflection signals, one can investigate the “unstable–metastable–stable” transition by monitoring the change of  $R$ . Five parallel experiments were performed to check whether  $R$  drops upon external disturbance at certain evaporation times and whether  $R$  recovers via placement. The blue zone can be attributed to the “unstable” state, because colloidal particles continuously precipitate out of the supersaturated solution to form more or larger colloidal crystals, which raise the  $R$  monotonically. The green zone corresponds to the “metastable” state because the solvent wrapped colloidal crystals can maintain ordered structure for

quite a long time (from 2 to 300 min). Such colloidal crystals will disassemble immediately by external disturbance, but they form again quickly when they are kept untouched for a while (Figure 1c). The red zone is attributed to the “stable” state, because most or all solvents have been evaporated and the colloidal crystal will not change structure even if an external disturbance is applied, so that  $R$  maintains the same value (Figure 1d). It should be noted that the “V” shaped evolution of  $R$  crossing the metastable and stable zone is caused by first reduction and then increase in the difference of refractive index between  $\text{SiO}_2$  particles and the surroundings ( $n_{\text{EtOH}} = 1.36$ ;  $n_{\text{EG}} = 1.43$ ;  $n_{\text{SiO}_2} = 1.46$ ), when ethanol residual and ethylene glycol are gradually evaporated. Otherwise, it should be a flat line throughout the evaporation process. It is also worth noting that high temperature ( $90\text{ }^{\circ}\text{C}$ ) is used to accelerate the evaporation, and the metastable plateau can actually be even longer at room temperature.

Reversible assembly and disassembly are the most important characteristics of metastable CCAs. Because of its intrinsic unfixed structure, a metastable CCA can easily disassemble into particles upon agitation, flow, convection, or vibration, while the particles in the supersaturated state will spontaneously precipitate to form a metastable CCA again in the absence of external disturbances. Accordingly, the peak in the reflection spectrum of the CCA will disappear due to disassembly and gradually return during reassembly. Figure 2b depicts the

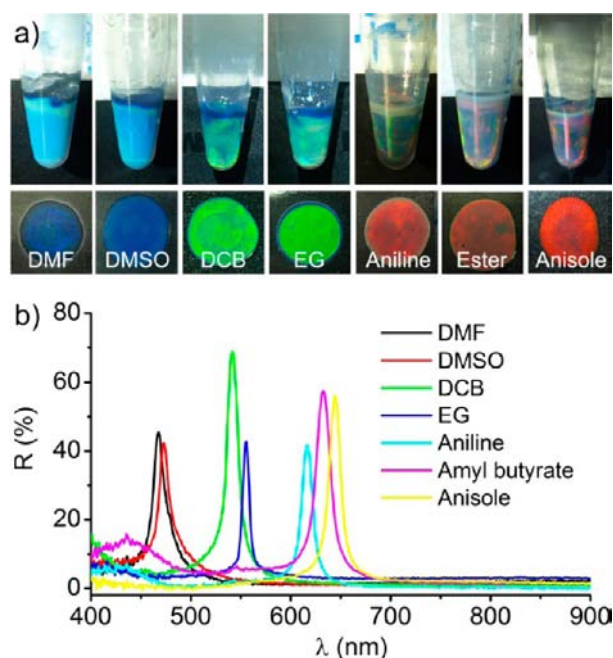


**Figure 2.** (a) Reversible transformation between supersaturated solution of particles and metastable CCAs. (b) Reflection intensity ( $R$ ) drops as the cover glass sandwiching the metastable CCA is touched and recovers as the solution sits undisturbed.

evolution of reflection intensity ( $R$ ) at  $530\text{ nm}$  in  $10\text{ s}$  intervals during three continuous disassembly assembly processes for a typical metastable CCA with a  $\Phi_{\text{SiO}_2}$  of  $0.4$ . The reflection intensity immediately dropped to  $8\%$  when the upper glass slide was touched to induce a relative displacement between the two glass slides sandwiching the crystal suspension, and it gradually increased to  $70\%$  after  $2\text{ min}$  as the sandwiched solution was placed undisturbed. It should be noted that the difference in recovery time (several to  $10\text{ min}$ ) for different samples is small, and the recovery time for a specific sample is repeatable in most cycling tests. The switching not only verifies the characteristics of the “metastable” CCAs but also proves that the transition between unstable supersaturated solutions of particles and metastable CCAs is reversible and fully controllable.

**3.2. Solvent and Particle Volume Fraction.** The metastable CCAs can be prepared in many target solvents with high boiling points and low viscosities. Figure 3 shows





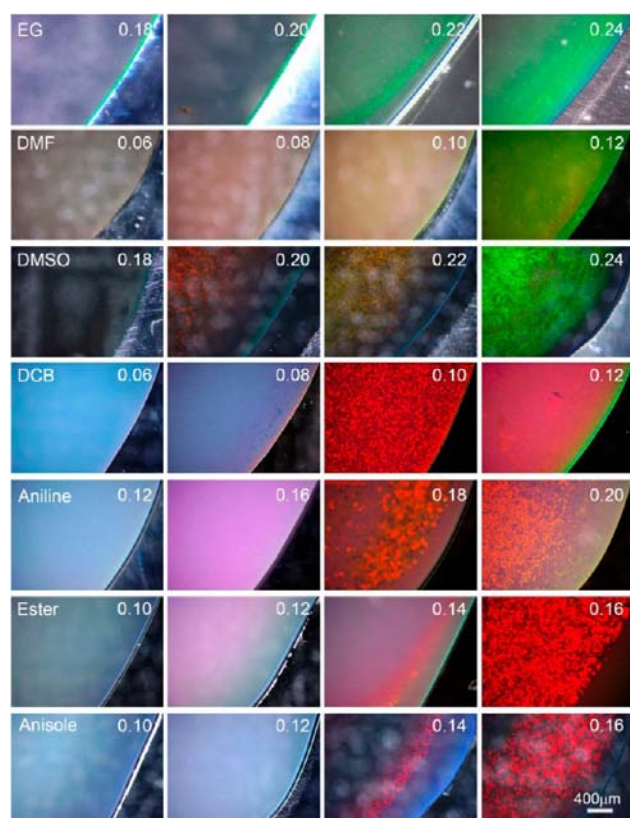
**Figure 3.** (a) Photos and (b) reflection spectra of metastable CCAs formed in different solvents. Designed particle volume fractions are all 0.3, and the average particle diameter is 189 nm, except for those in DMF and DMSO (135 nm).

various liquid CCA suspensions stored in tubes and sandwiched between glass slides. It should be noted that 0.05% of carbon powder is only added to increase the color contrast of the CCA suspensions stored in tubes,<sup>25</sup> and no carbon was added for the liquid films and reflection measurements. The narrow reflection peaks with full widths at half-maximum (FWHM) of 10–20 nm prove that highly ordered colloidal microcrystals can form in dimethylformamide (DMF), dimethyl sulfoxide (DMSO), dichlorobenzene (DCB), ethylene glycol (EG), aniline, amyl butyrate, and anisole. As shown in Table 1, these solvents all have high boiling points, so they remain in the liquid state when the good solvent from the original particle solutions is evaporated. They also have a low viscosity, which favors the Brownian motion of the particles in the highly concentrated state and thereby the colloidal assembly. Conversely, glycerol is not a suitable “target solvent” despite its similarities to ethylene glycol, because its high viscosity inhibits the Brownian motion critical for assembly.

It is not surprising to see the particle assembly occur in polar solvents such as EG, DEG, DMF, or DMSO. However, with the addition of a small amount of oleylamine, the particles could be dispersed in nonpolar benzenes, esters, and ethers and also assembled into CCAs, which provides an efficient method for assembling hydrophilic particles directly in nonpolar solutions. Here, the addition of oleylamine has two major functions. First, the polar–polar interaction between Si–OH and –NH<sub>2</sub> groups induces the adsorption of oleylamine molecules on the surface of the SiO<sub>2</sub> particles, which prevents agglomeration and enhances their stability in nonpolar solvents. Second, the addition of surfactant molecules to nonpolar dispersions can produce small reverse micelles, which enhance the charge separation of SiO<sub>2</sub> particles (particle–OH → particle–O<sup>−</sup> + H<sup>+</sup>) by stabilizing their counterions (H<sup>+</sup>) in the cores of the micelles.<sup>26</sup> Generally, charge separation is extremely difficult to obtain in nonpolar solvents, leading to a common expectation

that electrostatic repulsion is negligible in nonpolar solvents. However, with the introduction of surfactant molecules, strong electrostatic repulsion can be achieved due to enhanced charge separation, which certainly favors the assembly of particles.

Aside from proper solvents, the supersaturation state was another precondition to form solvent wrapped CCAs, which actually requires a high particle volume fraction in the target solvents. Here, metastable CCAs in EG were used to investigate the influence of  $\Phi_{\text{SiO}_2}$  upon assembly, and optical microscope images and reflection spectra were recorded (after resting each sample for 10 min) to determine the minimal volume fraction to form metastable CCAs. As  $\Phi_{\text{SiO}_2}$  was finely tuned from 0.18 to 0.2, 0.22, and 0.24, the colloidal microcrystals would form when  $\Phi_{\text{SiO}_2}$  reached 0.22, suggesting that 0.2 could be the critical volume fraction for particles in EG at room temperature (Figure 4). This observation leads to two conclusions: one is

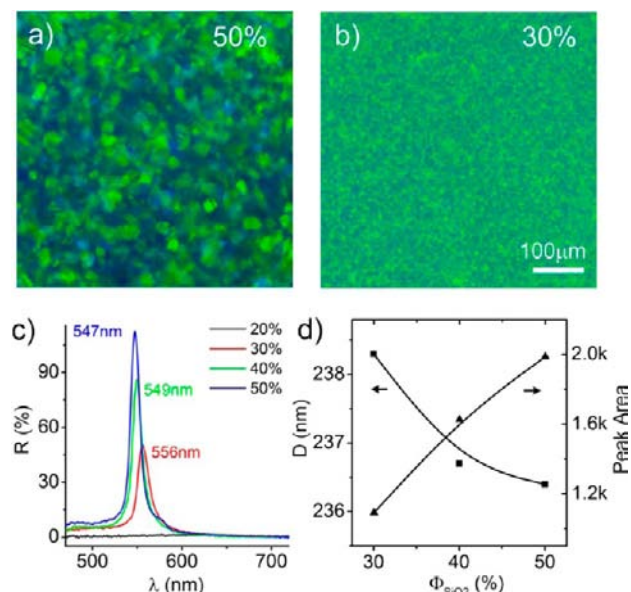


**Figure 4.** Metastable CCAs formed in different target solvents when  $\Phi_{\text{SiO}_2}$  exceeds the critical value.

that the colloidal particles are supersaturated at room temperature when the volume fraction is larger than 0.2; the other is that the precipitation of particles will stop if the volume fraction is below 0.2. The minimal volume fractions necessary for the formation of metastable CCAs in other solvents were determined by similar procedures. Figure 4 shows that SiO<sub>2</sub> particles tend to precipitate into metastable CCAs in nonpolar solvents even if  $\Phi_{\text{SiO}_2}$  is small (0.08–0.12), and they will form metastable CCAs in polar solvents only if  $\Phi_{\text{SiO}_2}$  is much larger (0.18–0.2). This is consistent with the high solubility of SiO<sub>2</sub> particles in polar solvents.

When the particle volume fraction exceeds the critical value, it has great influence upon the number and domain size of

colloidal microcrystals. As  $\Phi_{\text{SiO}_2}$  is increased to 0.3, numerous colloidal microcrystals with diameters of 2–5  $\mu\text{m}$  precipitate out of the supersaturated solution. When  $\Phi_{\text{SiO}_2}$  is further increased to 0.4 and 0.5, the number of CCAs decreases but the microcrystal size increases to 23–35  $\mu\text{m}$  (Figure 5). By



**Figure 5.** (a, b) Microscope images of metastable CCAs formed in supersaturated solutions with different  $\Phi_{\text{SiO}_2}$ . (c) Corresponding reflection spectra and (d) evolution of interparticle distances and reflection peak area as  $\Phi_{\text{SiO}_2}$  was increased.

examining many samples, we found the size of the microcrystals to be mostly within several tens of micrometers. Here, the size was counted as the diameter of the circumscribed circle of the microcrystals. In very few cases, the microcrystals grow up to 100  $\mu\text{m}$ . The interparticle distances ( $D$ ) inside the microcrystal can be calculated by eq 1, where  $m$  is the diffraction order,  $\lambda$  is the reflection wavelength, and  $n_{\text{total}}$  is the average refractive index of the whole suspension. In this work,  $m$  is equal to 1,  $\lambda$  can be directly obtained from the reflection spectra, and  $n_{\text{total}}$  can be calculated from the refractive index of each component and its volume fraction (eq 2). As  $\Phi_{\text{SiO}_2}$  was increased from 0.3 to 0.4 to 0.5, the corresponding interparticle distance ( $D$ ) was calculated to be 238.35, 236.65, and 236.64 nm, which shows that the crystal structures are very similar in all three cases (Figure 5d; Supporting Information, section 4). On the other hand, the reflection peak area quantifying the amount of ordered structures increases with the rise of  $\Phi_{\text{SiO}_2}$ , which is consistent with the enlargement of the grain size for CCAs produced in high- $\Phi$  precursors.

$$m\lambda = (8/3)^{0.5} D n_{\text{total}} = 1.633 D n_{\text{total}} \quad (1)$$

$$n_{\text{total}} = n_{\text{EG}}\phi_{\text{EG}} + n_{\text{SiO}_2}\phi_{\text{SiO}_2} + n_{\text{EtOH}}\phi_{\text{EtOH}} \quad (2)$$

**3.3. Formation Mechanism of Metastable CCAs.** Based on the discussion of the roles of solvents, supersaturation, and particle volume fraction, we can attribute the formation of metastable CCAs to the supersaturation induced precipitation of particles and thereafter the colloidal assembly induced by the balance of attractive and repulsive interactions. (1) The first question regarding the mechanism of the aforementioned

process is why the particles precipitate out of the solution. Since the overall solution is electrically neutral, the suspension is composed of negatively charged particles and their counterions. As  $\Phi_{\text{SiO}_2}$  rises to a supersaturated level, the number of counterions and the solution's ionic strength greatly increases as well, which weakens the electrostatic repulsions and causes the precipitation. (2) Why do the particles aggregate into ordered structures but not randomly stacked precipitates? It is due to the balance between interparticle attraction and repulsion.<sup>27</sup> Generally, the interaction between colloidal particles can be described by DLVO (Derjaguin–Landau–Verwey–Overbeek) theory as a combination of van der Waals attraction and electrostatic repulsion. DLVO theory predicts that a pair of like-charged colloidal particles in an electrolyte solution should experience a purely repulsive screened electrostatic (Coulombic) interaction.<sup>28</sup> However, this was challenged by recent experimental evidence that the interaction between like-charged particles can have a long-range attractive component in more concentrated suspensions and for particles confined by charged glass walls.<sup>29</sup> Although the strong long-range attraction between like-charged particles only takes effect within several micrometers away from the charged glass wall and it is only responsible for the stabilization of several layers of colloidal crystals, the formed several particle layers can act in a manner comparable to the glass wall in providing a geometrical confinement required for attractive interaction, which eventually leads to the precipitation of three-dimensional colloidal crystals. From this viewpoint, the formation of ordered structure in this work was caused by the balance between long-range attraction and electrostatic repulsion of neighboring like-charged particles. van der Waals attraction is not considered here, because the surface-to-surface distance between two neighboring particles in the colloidal crystal is determined to be 50–80 nm (Supporting Information, Table S2), which apparently exceeds the effective distance of van der Waals interaction. (3) The last question regarding the mechanism is why the growth of metastable colloidal crystals is self-limiting, leaving behind a stable two phase mixture of microcrystals and homogeneous particle suspensions? As 50–82% (see calculations later) of the  $\text{SiO}_2$  particles precipitate into colloidal crystals, the number of counterions and the solution's ionic strength decrease, so the screened electrostatic repulsion experienced by the particles greatly enhances, which overcomes the long-range attraction and prevents the free particles from further deposition.

The formation of metastable CCAs can be understood as a microscopic phase separation process based on the evolution of particle volume fraction in the whole system, the colloidal crystal and the organic liquids. At the beginning, the supersaturated solution is a homogeneous dispersion, in which  $\Phi_{\text{SiO}_2}$  is uniform throughout the system. If  $\Phi_{\text{SiO}_2}$  is larger than 0.2, the particles start to precipitate out of the solution to form colloidal crystal seeds, so that the dispersion will microscopically separate into two phases: one “crystal phase” with orderly stacked particles and one “liquid phase” with particles dispersed in solution, even if the solution itself is seemingly homogeneous. The particles in the liquid phase will continue to precipitate and deposit onto the CCA seeds until  $\Phi_{\text{SiO}_2}$  decreases to 0.2. At the same time, the CCAs become larger during seeded growth, and finally these two phases reach equilibrium (Supporting Information, Figure S1). Because of the metastability of solvent wrapped CCAs, this equilibrium is



easy to break, so the particles may disperse back into the solution, which recovers to the original  $\Phi_{\text{SiO}_2}$ . The supersaturation induced precipitation is a general phenomenon that should work for many other target solvents and colloidal particles. For instance, we have also been successful in using  $\text{CeO}_2$  colloidal particles as building blocks to form metastable CCAs.

Theoretical calculations of the volume fraction of the crystal phase in the overall suspension ( $V_{\text{crystal}}/V_{\text{total}}$ ) and the distribution ratio of particles in the crystal phase ( $f_{\text{crystal}}$ ) provide further verification of microscopic phase separation and supersaturation induced precipitation (Supporting Information, section 4). Because of the residual good solvent after evaporation, the actual particle volume fraction ( $\phi_{\text{SiO}_2}$ ) of the overall suspension was determined to be 0.26, 0.308, and 0.327 for the solutions whose  $\Phi_{\text{SiO}_2}$  was initially designed to be 0.3, 0.4, and 0.5. The particle volume fraction in the liquid phase ( $\phi_{\text{liquid}}$ ) was estimated to be 0.2 because it was the critical concentration for precipitation. The particle volume fraction in the crystal phase ( $\phi_{\text{crystal}}$ ) can be calculated according to the average particle diameter (189.4 nm) and interparticle distances (238.35, 236.65, and 236.64 nm) using eq 3, where 0.7405 is the volume fraction of spheres in close-packed structures. Therefore,  $\phi_{\text{crystal}}$  was calculated to be 0.372, 0.380, and 0.380, which confirms the existence of intervals between particles in the metastable CCAs. The relatively high particle volume fraction in the crystal phase ( $\phi_{\text{crystal}} > \phi_{\text{SiO}_2}$ ) and the lower volume fraction in the liquid phase ( $\phi_{\text{liquid}} < \phi_{\text{SiO}_2}$ ) confirm the microscopic phase separation and reveal the nature of the assembly process. Using eqs 4 and 5, one can find that colloidal microcrystals make up 35%, 60%, and 70% of the total volume of the suspension as  $\Phi_{\text{SiO}_2}$  increases from 0.3 to 0.5. Further calculations using eqs 6 and 7 indicate that 50%, 74%, and 82% of the silica particles assemble into metastable CCAs. The calculations in sections 3.2 and 3.3 suggest that with an increase of the designed  $\Phi_{\text{SiO}_2}$ , more silica particles precipitate to form colloidal crystals with larger sizes and volume ratios, but the lattice spacing of the microcrystals scarcely changes.

$$\phi_{\text{crystal}} = (189.4/D)^3 0.7405 \quad (3)$$

$$\phi_{\text{SiO}_2} = \phi_{\text{crystal}} V_{\text{crystal}}/V_{\text{total}} + \phi_{\text{liquid}} V_{\text{liquid}}/V_{\text{total}} \quad (4)$$

$$V_{\text{crystal}}/V_{\text{total}} + V_{\text{liquid}}/V_{\text{total}} = 1 \quad (5)$$

$$\begin{aligned} f_{\text{crystal}} &= (\phi_{\text{crystal}} V_{\text{crystal}})/(\phi_{\text{SiO}_2} V_{\text{total}}) \\ &= \phi_{\text{crystal}}/\phi_{\text{SiO}_2} (V_{\text{crystal}}/V_{\text{total}}) \end{aligned} \quad (6)$$

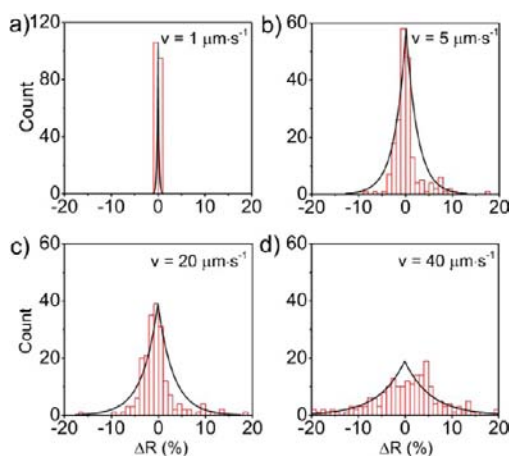
$$f_{\text{liquid}} = \phi_{\text{liquid}}/\phi_{\text{SiO}_2} (V_{\text{liquid}}/V_{\text{total}}) = 1 - f_{\text{crystal}} \quad (7)$$

**3.4. Sensing Weak Mechanical Forces.** Thanks to the good control and reproducibility in their synthesis, some unique applications of metastable CCAs suspended in solution become feasible. It has already been demonstrated that these metastable colloidal crystals can be fixed in a polymer matrix through polymerization if the solvent is replaced by an appropriate monomer, which produces useful materials for sensing and molecular recognition.<sup>30–35</sup> However, few researchers noticed that the metastable CCA itself can also be an interesting responsive material, which changes its

photonic properties due to the fluidity of incorporated liquids as opposed to the deformation of an elastic polymer matrix. Although solid responsive photonic crystals are more popular due to their convenient operation, this liquid responsive material also has its intrinsic advantages, such as fast response and ease in changing the photonic structure.

As a demonstration, we utilize the reflection fluctuation ( $\Delta R = R_{t+1} - R_t$ ) of a metastable CCA to sense the slow motion of glass slides and the resulting weak frictional or shearing force on the scale of  $10^{-6}$  to  $10^{-8}$  N. Here, the metastable CCA suspension was sandwiched between two hydrophobic glass slides, where the bottom slide was fixed and the upper one was pulled with a constant speed from 0 to  $40 \mu\text{m}\cdot\text{s}^{-1}$ . A reflection probe perpendicular to the glass slides was used to record the reflection with a step size of 1 s (Supporting Information, Figure S2). It should be noted that the optical probe collected reflection signals within a circular region with a diameter of about 4 mm. Therefore, although the metastable microcrystals move during the pulling process, the object studied at  $t$  and  $t + 1$  s can be regarded as the same, considering that the displacement was much smaller than the range of the probe. For each pulling speed, the reflection fluctuations ( $\Delta R = R_{t+1} - R_t$ ) within every second were counted to plot the distribution of  $\Delta R$ .

The reflection of the metastable CCA is very sensitive to the moving speed of glass slide and the shearing force applied to the liquid suspension. Figure 6 shows that slow pulling led to



**Figure 6.** Distribution of reflection intensity fluctuations ( $\Delta R = R_{t+1} - R_t$ ) for a metastable CCA sandwiched between two glass slides becomes broader as the upper slide moves faster.

small reflection fluctuations and a very narrow distribution of  $\Delta R$  because the microdisplacement in 1 s did not seriously interfere with the colloidal assembly. Fast pulling caused a random  $\Delta R$  and thereby a broad distribution of  $\Delta R$  as the interference was amplified. According to the definition of viscosity and the balance between frictional and shearing force, this internal relationship can also be extended to sense the strength of the frictional and shearing forces applied to the upper glass slides ( $9.67 \times 10^{-8}$  to  $3.87 \times 10^{-6}$  N), that is weak or strong forces cause a narrow or broad distribution of  $\Delta R$  (Supporting Information, section 5). These colloidal microcrystals are uniquely sensitive to weak environmental disturbances, because changing the photonic structure of metastable CCAs requires much less energy than that consumed in the tuning of traditional responsive photonic

crystals. From this viewpoint, it may be further extended to the sensing of weak vibrations.

#### 4. CONCLUSIONS

In summary, solvent wrapped “metastable” colloidal crystals were prepared by the supersaturation induced precipitation and assembly of monodisperse particles in organic solvents. The synthesis provides a convenient and universal route to generate metastable CCAs in polar and even nonpolar solvents with monodisperse and mutually repulsive particles. Nonvolatile and nonviscous solvents, as well as a supersaturated particle volume fraction, are preconditions to form these metastable CCAs. The metastable colloidal crystals are built based on the balance between long-range attraction and electrostatic repulsion of neighboring like-charged particles, and the evolution of reflection intensity during evaporation proves that these crystals can exist for several hours at 90 °C and even longer at room temperature. The formation of metastable CCAs can be understood as a microscopic phase separation process, in which most particles form “crystal phase” assemblies and the rest remain in the “liquid phase” suspension. These two phases reach a balance when the particle volume fraction in the suspension decreases to the minimum value required for precipitation. Since little energy is required to change the structure of a metastable CCA, it can be affected by weak external disturbances and can be used to sense the slow movement of glass slides ( $0\text{--}40\ \mu\text{m}\cdot\text{s}^{-1}$ ) and weak frictional and shearing forces ( $10^{-8}$  to  $10^{-6}$  N). The current work reveals a new pathway to develop responsive photonic materials, and the replacement of the target solvent with proper monomers combined with polymerization can convert a metastable CCA into a stable one and create even more useful new materials for sensing, display units, and antifraud labels.

#### ■ ASSOCIATED CONTENT

##### Supporting Information

Discussion about solvent selection and its influence upon particle repulsion, crystal growth of metastable CCAs, the calculation of particle distribution ratio in two phases, and details of force sensing. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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##### Notes

The authors declare no competing financial interest.

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