

Microstructures Design of the Assembly of Monodisperse Polystyrene Microspheres via Alternative Current Electric Field

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ABSTRACT

Nanomaterials as building blocks offer a promising route for material preparation. And to this purpose, controllable assembly of nanomaterials and microstructure design of the assembly are of great significance. Herein, the assembly of monodisperse polystyrene microspheres under alternative current electric field was applied as a model system. The conditions, such as voltage and frequency of the electric field, surface charge of the spheres, solvents and salt concentration, were adjusted to obtain different microstructures of the assembly like chain, island and flower. Preliminary results indicates that surface states of the spheres plays a key role in the final structures while low dielectric constants of the solvents and high salt concentration only caused agglomeration of the microspheres. This work will bring new insight into the assembling process of the nanomaterials as well as understanding the mechanism controlling the microstructures of the assembly.

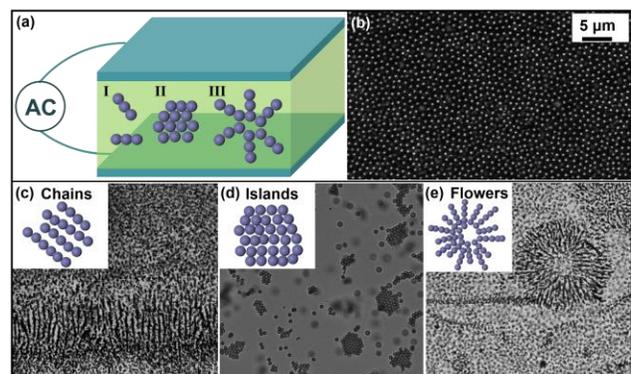
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1 INTRODUCTION

The recent development of particle synthesis enables the revolution in novel nanoparticles and colloidal building blocks.^[1,2] Bottom-up assembly of these building blocks into various well-defined structures with different functionality offers a promising route for both material preparation and understanding the assembly mechanisms at atomic and molecular level.^[3-7] And to this purpose, controllable assembly of colloidal building blocks and the microstructure design of the assembly are of great significance.^[6] However, the mechanism of the assembling process is complicated and still unclear and direct observation of the assembling is difficult for nanoparticles with small size. And therefore, sub-micro particles with suitable size and shapes will provide an ideal platform to investigate the assembling process and finally control the structures.

Field-induced assembly of the colloidal building blocks offers a convenient and simple pathway to realize various structures.^[3,5] And so far, great advances have been

achieved in alternative current (AC) field induced assembly of both anisotropic and isotropic colloidal building blocks due to the easy accessibility of AC field and the precise tuning of forces exerted on the colloidal building blocks and the fluid medium by the field. Velev's group investigated the dielectrophoretic assembly of micrometer-sized metallodielectric Janus particles in water (e.g., gold-coated PS microspheres) under AC fields of both low frequency (<10 kHz) and high frequency (>10 kHz). Different morphology such as 3D bundles, 2D crystallization and chains was obtained with varied electric field strength and frequency.^[8,9] Vutukuri et al. obtained bead chains with tunable stiffness using monodisperse polymethyl-methacrylate (PMMA) particles in cyclohexyl bromide relying on the dipolar interactions induced by external AC fields in combination with long-range electrostatic repulsion. The chains aligned in the direction parallel to the external field in a head-to-tail arrangement with the length tuned easily by the field strength.^[10] Recently, Wu et al. developed a versatile method for creating different colloidal "molecules" with isotropic monodisperse polystyrene (PS) particle. Oligomers with different "molecular weight" and hierarchically non-close-packed structures were observed by changing field strength, frequency, particle concentration and salt concentration via dipolar and dielectrophoretic interaction.^[11] Single monodisperse PS microspheres exhibiting various structures under AC field motivates us to carry out further investigation on the intrinsic mechanism of the assembly of PS microspheres.



Scheme 1. (a) The typical experimental setup for the colloidal assembly of microspheres under AC field. (b)

Optical photograph of the original colloidal PS microspheres. (c-e) Different assembly obtained with different conditions.

Herein, the assembly of monodisperse PS microspheres under AC electric field was applied as a model system. The microspheres of about 1-2 μm in diameter enable us to directly observe the dynamic process. And the microstructures of the assembly was adjusted by changing the assembling conditions, such as voltage and frequency of the electric field, solvents and salt concentration. And various structures were obtained like chain, island and flower. (Scheme 1) We believe this work will bring new insight into the assembling process of the colloidal particles as well as understanding the mechanism dominating the microstructures of the assembly.

2 EXPERIMENTAL

2.1 Materials

Styrene (St) was purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China) and purified by distillation under reduced vacuum to remove inhibitor before use. The initiator, azobisisobutyronitrile (AIBN) was purified by recrystallization from water. Methanol, polyvinyl pyrrolidone (PVP), dimethyl sulfoxide (DMSO) were brought from Aladdin-reagent. Indium-tin-oxide (ITO) glass slides were obtained from Sigma-Aldrich, Inc. The slides were sonicated in propanol and acetone for 10 min respectively before use.

2.2 Preparation of monodisperse colloidal microspheres

The monodisperse colloidal PS microspheres was synthesized via dispersion polymerization. In brief, a certain amount of PVP and methanol were added into a flask and stirred at 200 r/min. The solution was purged with N_2 for 1 h and then the temperature was raised to 40 $^\circ\text{C}$. Afterward, the monomer St and the initiator AIBN were added to the flask and the solution was allowed to react for 12 h at 70 $^\circ\text{C}$. A 200-mesh screen was used to filter the agglomeration and finally, the colloidal suspension of PS microspheres was obtained.

2.3 Colloidal assembly of microspheres under AC field

The cross-sectional view of the experiment device is shown in Scheme 1a. The colloidal suspension of monodisperse PS microsphere was sandwiched between two ITO electrodes. The electrodes were separated by a polymer gasket (Surlyn) with about fifty micrometers. And two conductive wires were attached on the ITO and connected with the Zahner Zennium electrical workstation,

which was used as the AC electric generator. The device was placed directly under the optical microscope.

2.4 Characterization

The dynamic assembling process was observed with an upright microscope (Zeiss AXIO Scope A1) attached with an AxioCam MRc5 CCD. The shape and monodispersity of as-prepared PS microsphere were characterized by a scanning electron microscope (SEM, S-4800 Hitachi).

3 RESULTS AND DISCUSSION

The brief illustration of the experiment device is shown in Scheme 1a. The AC field is applied perpendicular to the ITO electrodes, and the gap between the two electrodes is about 50 μm , which is much large than the diameter of the PS particles.

The typical scanning electron microscope (SEM) image of PS microspheres is shown in Figure 1a. As can be seen, the as-prepared PS microspheres are spherical in shape and monodisperse with a diameter of about 1.5 μm . The optical image of their aqueous suspension with 1.5 vol% without AC field is shown in Figure 1b. The suspension is uniform without any agglomeration. The particle concentration shown in Figure 1b is much lower than the actual concentration due to the fact that the density of PS is higher than water and the Brownian movement and electrostatic repulsion are not strong enough to stabilize the particles with large size, leading to their settling with gravity. The particles with a diameter of about 3 μm settle down quickly while those of 1 μm cannot be observed clearly with the optical microscope. And therefore, the PS particles with a diameter of about 1.5 μm serve as a suitable choice to study their assembly under AC field.

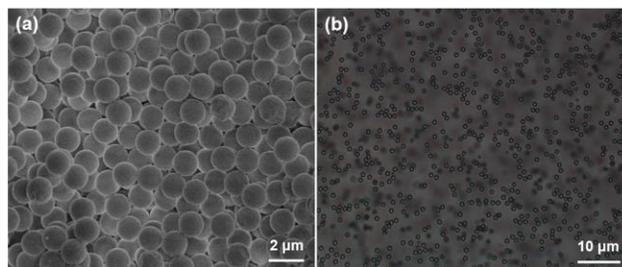


Figure 1. (a) The typical SEM image of the as-prepared PS microspheres with a diameter of about 1.5 μm . (b) The optical image of the aqueous suspension of the PS microspheres without AC field.

In our experiments, we observed that when the frequency of the AC field is low than 50 Hz, the solvent is prone to electrolyze with high voltage (12.5 V), while for high frequency larger than 1 kHz, the movement of the PS particles is quite slow even with a high voltage (25 V). Therefore, we adjusted the voltage between 10 V and 25 V with the electric-field strength between 0.2 $\text{V } \mu\text{m}^{-1}$ and 0.5 $\text{V } \mu\text{m}^{-1}$.

As shown in Figure 2a, when an AC field is exerted on the aqueous suspension of the PS microspheres, a combination of chains, dimers and other random structures formed despite the voltage and frequency. Besides, the movement of the particles slowed down with prolonging AC field, and finally were fixed on the electrodes. This can be explained by the fact that the gravity could not be negligible in this case and the particles gradually settled and finally electrodeposited on the electrodes, as in the case of direct current (DC) field.^[12,13] This phenomenon is different from those in the previously reported literature and it can be ascribed by the surface charge of the particles.^[11] Different synthetic procedure will result in PS particle with different surface properties. And in some reports, the ITO electrodes are thoroughly cleaned and even modified with other agents to prevent the adhesion of the particles on them.^[11,14] We have also cleaned the electrodes and modified them with poly sodium 4-styrene sulfonate, however, the adhesion and settlement of the PS particle cannot totally prevent with aqueous suspension. And therefore, we employed DMSO as the solvent, which possesses a higher density than water. The corresponding optical image of the assembly is shown in Figure 2b at 1 kHz and 12.5 V with a concentration of 0.22 vol%. Chain structures were formed in this conditions. The most chains are short and contain three to five single particles in length and one particle in width. These chains are stable and move randomly under the AC field. When the AC field was removed, the chains slowly disassembled in to particles. By heating the electrodes with hot air, the chains can be fixed even when the field is removed as demonstrated in the literature.^[10] Interestingly, instead of being parallel with the AC field, the chains are perpendicular to the field, which is contradictory with the previous report, in which monodisperse PMMA particles were dispersed in cyclohexyl bromide.^[10] The intrinsic mechanism for the difference is still under investigation. We further studied the assembly of concentrated DMSO suspension of PS particles (0.44 vol%). And island structures were obtained instead of chains structures. These close-packed structures are perpendicular with the AC field and gradually agglomerate with each other to form larger structures with prolonging AC field. The solvent effect was also investigated through a combination of DMSO and water. The corresponding optical image is shown in Figure 2d. Similar chain structures were obtained at low voltage (100 Hz). The chains are longer than those in pure DMSO suspension and most of them contain more than five particles in length, though still one particle in width. Besides, we also studied the salt effect on the assembly by adding sodium chloride into the suspension. However, low concentration ($<10^{-4}$ M) of the salt showed little effect on the assembly while high concentration ($>10^{-4}$ M) leads to the coagulation of the particle due to the neutralization of the surface charges of the particles.

Different solvents possess different dielectric constants. And the difference of the dielectric constant between solvent and colloidal particles results in the induced dipolar

moments of the particles. The dipolar interaction along with the electrostatic interaction leads to rich phase behaviors of the assembly.^[15,16] These factors can be tuned by the size and surface properties of the particles, solvents, salt concentrations and the external fields. The external factors have been examined as shown above, and therefore we further investigated the effects of particle properties. We synthesized poly methacrylic acid (PMAA) modified PS microspheres to increase the surface charge of the particles.

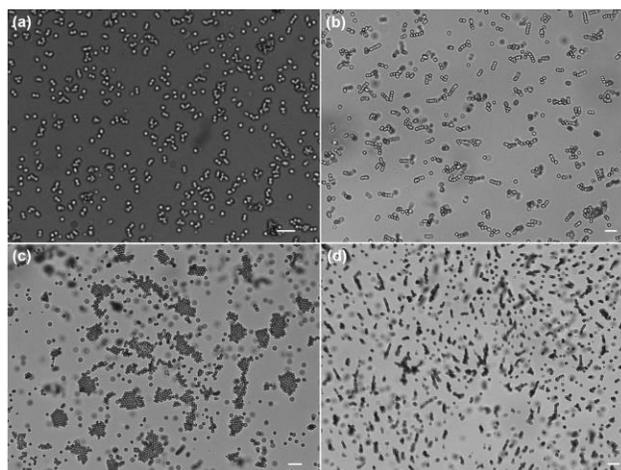


Figure 2. (a) Optical image of the aqueous suspension of PS microspheres at 1 kHz and 5V AC field. (b) Chain structures formed in DMSO at 1 kHz and 25 V. (c) Island structures formed in DMSO at 1 kHz and 12.5 V. (d) Chains structures formed in DMSO and water (1:1 vol) at 12.5 V and 100 Hz. (Scale bar: 10 μ m)

After the modification, we found that the aqueous suspension of PMAA-PS microspheres assembled under the AC field. And as shown in Figure 3a, a flower structure formed, which consists of tens of chains. In a lower magnification (Figure 3b), several flower structures can be observed, and some even fuse into a more complicated structure. Still, the structures are perpendicular to the AC field. Such flower structures herein are reported for the first time. And they cannot be explained by simply considering the dipolar and electrostatic interactions and their formation mechanism is still under investigation. By increasing the voltage of the field, the flower structure disassembled into random long chains, while increasing the frequency caused the formation of random short chains. Obviously, the modification with PMAA increased the surface charges of the microspheres and therefore, intensified the interaction of the AC field on the particles.

The interaction between chains are weakened when the high electric field strength is applied, leading to the damage of the flower structures and increased frequency has a strong effect on the dipolar moment of the particles, causing the break of long chains into short chains.

And interestingly, the chain structures were observed to accumulate in the interface between liquid and air. The chains are parallel to each other and perpendicular to the

interface. The accumulation structures resemble the shape of the interface, which may be applied to prepared specific assembly with desired structures.

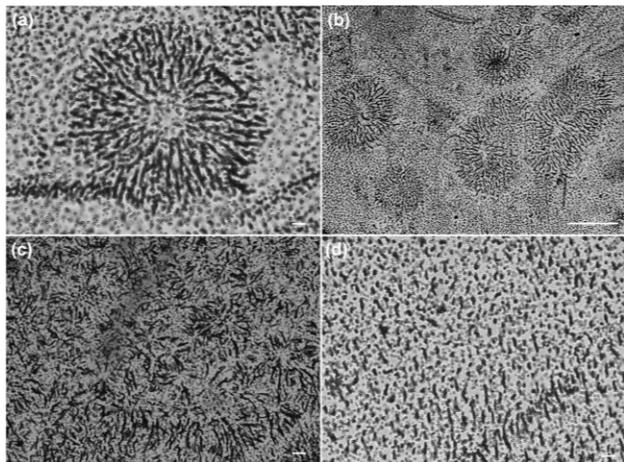


Figure 3. (a,b) The flower structures formed at 12.5 V and 100 Hz (scale bar: 20 μm and 200 μm respectively). And the random chains structures formed at (c) 25 V and 100 Hz and (d) 12.5 V and 1000 Hz.

This assembly process is similar to the formation of proteins. The microspheres assemble into chain structures (primary structures), and the chain structures further form island structures and flower structures (secondary structures). These secondary structures may further form tertiary and quaternary structures. Further attempts can be focused on the assembly of different colloidal particles (such as PS, PMMA, SiO_2 microspheres) and specific surface modification may lead to the formation of richer structures and morphology.

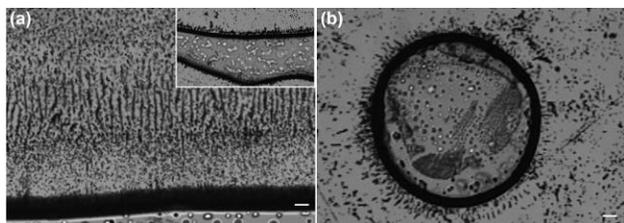


Figure 4. Chain structures accumulated in the interface between liquid and air. (Scale bar: 20 μm and 40 μm respectively)

4 CONCLUSION

In summary, we reported herein the microstructure design of the assembly of monodisperse polystyrene microspheres under the AC electric field. Various factors like voltage, frequency, solvent and surface charge of the particles are investigated and the final structures mainly depend on the surface properties and the dielectric constants of solvents and particles. Novel flower structures are obtained by the use of PMAA-PS microsphere. This

work will bring new insight into the assembling process of the colloidal particles as well as understanding the mechanism controlling the microstructures of the assembly. Further work can be concentrated on the surface modification of the particles and the electrodes, and mixed colloidal particles with different components and size can be applied to obtain more complicated structures and morphology.

5 ACKNOWLEDGEMENT

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REFERENCES

- [1] S. Sacanna, W. Irvine, P. Chaikin and D. Pine, *Nature*, 464, 575, 2010.
- [2] A. Walther and A. Muller, *Chem. Rev.*, 113, 5194, 2013.
- [3] A. Yethiraj and A. Blaaderen, *Nature*, 421, 513, 2003.
- [4] S. Yang, S. Kim, J. Lim and G. Yi, *J. Mater. Chem.*, 18, 2177, 2008.
- [5] A. Yethiraj, *Soft Matter*, 3, 1099, 2007.
- [6] S. Glotzer and M. Solomon, *Nat. Mater.*, 6, 557, 2007.
- [7] M. Trau, D. Saville, and A. Aksay, *Science*, 272, 706, 1996.
- [8] S. Gangwal, O. Cayre and O. Velev, *Langmuir*, 24, 13312, 2008.
- [9] S. Gangwal, A. Pawar, I. Kretzschmar, O. Velev, *Soft Matter*, 6, 1413, 2010.
- [10] H. Vutukuri, A. Demirovs, B. Peng, P. Oostrum, A. Imhof and A. Blaaderen, *Angew. Chem. Int. Ed.*, 51, 11249, 2012.
- [11] F. Ma, D. Wu and N. Wu, *J. Am. Chem. Soc.*, 135, 7839, 2013.
- [12] M. Ammam, *RSC Advances*, 2, 7633, 2012.
- [13] A. Krejci, I. Juan, and J. Dickerson, *ACS Appl. Mater. Interfaces*, 3, 3611, 2011.
- [14] F. Ma, S. Wang, L. Smith and N. Wu, *Adv. Funct. Mater.*, 22, 4334, 2012.
- [15] D. Prieve, P. Sides and C. Wirth, *Curr. Opin. Colloid In.*, 15, 160, 2010.
- [16] A. Hynninen and M. Dijkstra, *Phys. Rev. Lett.*, 94, 138303, 2005.