Supporting information

Kinetics–controlled Regulation for Homogeneous Nucleation and Growth of Colloidal Polymer and Carbon Nanospheres

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1. Materials and characterizations

Materials. Resorcinol, ethylamine (65 wt.%), ammonia solution (25 wt.%), formaldehyde (37 wt.%), and ethanol were purchased from Sinopharm Chemical Reagent Co., Ltd. Pluronic F127 was purchased from Sigma. All chemicals were used as received.

Characterizations. Scanning electron microscope (SEM) investigations were carried out with a Hitachi SU8220 instrument. Dynamic light scattering (DLS) measurements were carried out at 25 °C on a Malvern Zetasizer NanoZS Instrument (detection range: 3–3000 nm) equipped with ALV-5000/EPP Multiple Tau Digital Correlator and a JDS Uniphase 1145P 22 mW He-Ne laser (632.8 nm wavelength). The scattering angle was 90°, and the intensity autocorrelation functions were analyzed by the CONTIN method. The viscosity of solution was collected by the AR2000ex Rheometer. The measurements were conducted at 28 °C and concentric cylinder, the steady state flow step was applied at a shear rate from 10 s−1 to 100 s−1. The peak hold step was applied at a shear rate of 100 s−1 for 20 min. Nitrogen sorption isotherms were measured with an ASAP 3000 sorption analyzer (Micromeritics) at 77 K. All the samples were degassed at 200 °C for 4 h before the measurements. The surface areas (S_{BET}) were calculated using the Brunauer-Emmett-Teller (BET) method. Micropore size distributions (PSDs) were obtained from the adsorption branches of the isotherms with the density functional theory (DFT) method by the Autosorb-iQMP instrument. The surface tension was test at 28 °C by the K100C interface tensiometer (Krüss). The main text of the article should appear here with headings as appropriate.

2. Synthetic procedures

Synthesis of monodisperse polymer nanospheres

In a typical synthesis, 110 mg resorcinol were first dissolved in 200 ml X g L^{-1} F127 solution at 28 °C for 30 minutes. Then 146 μL formaldehyde was added into the solution and mixed for 15 minutes. After that, 22.5 mg ethylamine was added into this solution and mixed for 30 minutes. The solution became a white color. The 1.5 mmol ammonia were add to the final solution. The resultant solution was further heated to 80 °C accompanied with stirring 18 h. The obtained polymer nanospheres were purified with water for 3 times and denoted as PNSs-X. The corresponding carbon nanospheres was denoted as CNSs-X (X is the concentration of F127)

Synthesis of monodisperse carbon nanospheres

The carbon nanospheres (CNSs-X) were obtained by direct pyrolysis of PNSs-X at 500 °C for 2 h under an argon atmosphere.

3. Calculation of nucleation rate in a homogeneous process

The Gibbs free energy (ΔG_n) for forming a nucleus can be expressed as the sum of the volume energy (ΔG_V) and the surface energy (ΔG_A).

$$\Delta G_n = \Delta G_V + \Delta G_A \tag{1}$$

When the nucleus is spherical, the Gibbs free energy (ΔG_n)

$$\Delta G_n = \frac{4}{3}\pi r^3 \Delta G_v + 4\pi r^2 \gamma \tag{2}$$

γ is the surface tension, ΔG_v is the free energy of the transformation of per unit volume, r is the radius of spherical nucleus. The maximum value (ΔG_c), corresponds to the critical nucleus, r_c is the critical radius, so set $\dfrac{d(\Delta G_n)}{dr}\big|_{r=r_c} = 0$

$$\frac{d(\Delta G_n)}{dr}\Big|_{r=r_c} = 4\pi r^2 \Delta G_v + 8\pi r_c \gamma = 0 \tag{3}$$

Therefore,

$$r_c = \frac{2\gamma}{\Delta G_v} \tag{4}$$

From Equation 2 and 4,

$$\Delta G_c = \frac{4}{3}\pi \left(\frac{2\gamma}{\Delta G_v}\right)^3 \Delta G_v + 4\pi \left(\frac{-2\gamma}{\Delta G_v}\right)^2 \gamma = \frac{16\pi\gamma^3}{3(\Delta G_v)^2} \tag{5}$$

For a non-electrolyte system, the Gibbs–Thomson relationship can be written,

$$ln(S) = \frac{2\gamma V_m}{k_B T r_c} \tag{6}$$

The S is supersaturation ratio, k_B is the Boltzmann constant, T is the temperature, V_m is the polymer molecular volume. Set the Equation 6 into 4,

$$\Delta G_v = \frac{k_B T ln S}{V_m} \tag{7}$$

Set the Equation 7 into 5, the maximum value (ΔG_c),

$$\Delta G_c = \frac{16\pi\gamma^3}{3(\Delta G_v)^2} = \frac{16\pi\gamma^3 V_m^2}{3(k_B T ln S)^2} \tag{8}$$

If the J (the rate of increase of the number of particles N) is defined as the nucleation rate, it can be written in the Arrhenius form in terms of ΔG_c [Equation 8]

$$J = \frac{dN}{dt} = A exp\left[\frac{-\Delta G_c}{k_B T}\right] = A exp\left[\frac{-16\pi\gamma^3}{3k_B T(\Delta G_v)^2}\right] = A exp\left[\frac{-16\pi\gamma^3 V_m^2}{3k_B^3 T^3 (lnS)^2}\right] \tag{9}$$
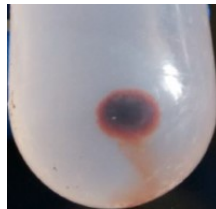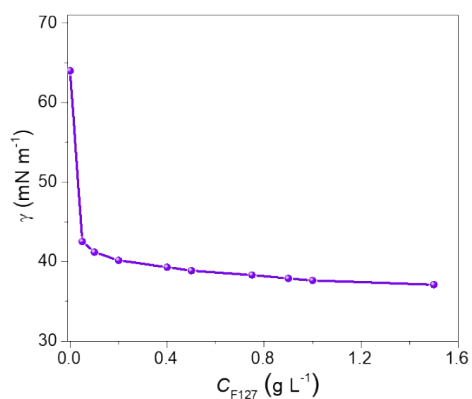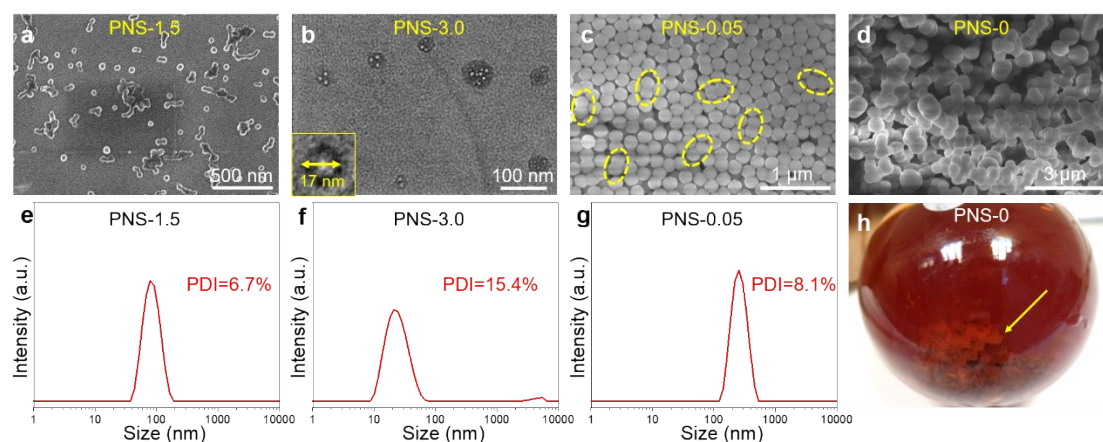
4. Supporting Figures

Fig. S1 The optical photograph of PNS-0.2 after high-speed centrifugation.

Fig. S2 The surface tension of the solution in different concentration of F127 before the addition of ethylamine.
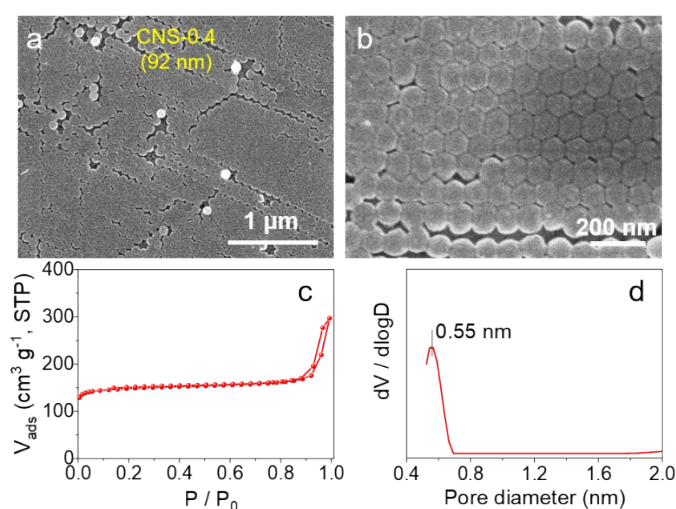

Fig. S3 (a) SEM image of PNSs-1.5, (b) TEM image of PNSs-3.0, SEM images of (c) PNSs-0.05 and (d) PNSs-0, the particle size distribution curves of (e) PNSs-1.5, (f) PNSs-3.0, and (g) PNSs-0.05, (h) photograph of PNSs-0 after reaction.
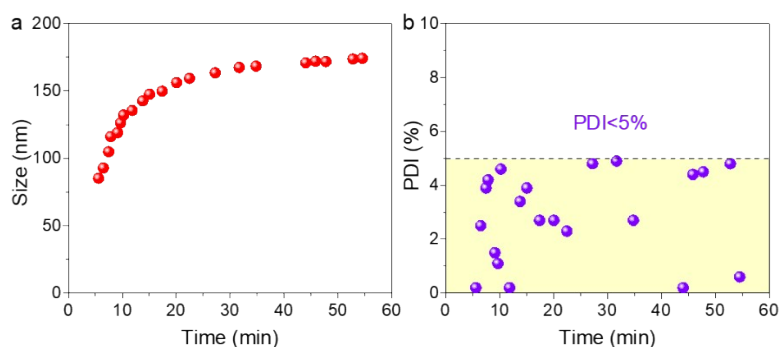
Fig. S4 (a) The average size and (b) particle dispersion index of PNSs-0.1 during the nucleation and growth process.
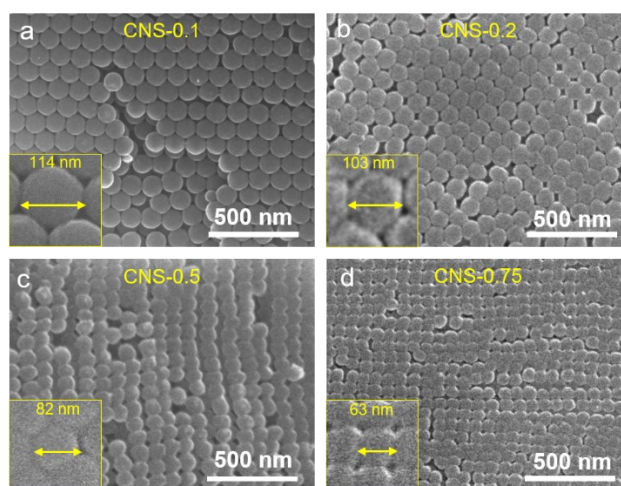
Fig. S5 SEM images of (a) CNSs-0.1, (b) CNSs-0.2, (c) CNSs-0.5, (d) CNSs-0.75.

Fig. S6 (a, b) SEM images of CNSs-0.4 and (c) Nitrogen sorption isotherm and (d) pore size distribution curve of CNSs-0.4 carbonized at 800 °C.

In this study, we reported a facile and operable kinetics–controlled method for the regulation of PNSs and corresponding CNSs with excellent monodispersity at nanoscale through precisely controlling the appropriate surface tension by changing the C_{F127}. Noteworthy, the size of PNSs can be varied from 148 to 59 nm and the size of the corresponding CNSs can be adjusted from 114 to 41 nm through regulating the surface tension from 41.2 to 37.6 mN m–1 during the nucleation process. Importantly, low viscosity facilitates the diffusion monomers and migration of particles, enabling the good monodispersity of nanospheres. Such superior monodispersed nanospheres would provide a material platform for fundamental structure-performance investigation on super-structure materials[1-2], electrochemistry, catalyst, adsorption, etc.

Reference:

1   H. Y. Wang, L. Zhou, H. M. Yu, X. D. Tang, C. Xing, G. C. Nie, H.   Akafzade, S. Y. Wang, and W. Chen, *Adv. Opt. Maters.*, 2022, 2200687.

2   Q. X. Zhong, J. Feng, B. Jiang, Y. L. Fan, Q. Zhang, J. X. Chen, and Y. D. Yin, *J. Am. Chem. Soc.*, 2021, **143**, 20513.