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Core–shell colloidal particles with dynamically tunable scattering properties†

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We design polystyrene–poly(*N*′-isopropylacrylamide-*co*-acrylic acid) core–shell particles that exhibit dynamically tunable scattering. We show that under normal solvent conditions the shell is nearly index-matched to pure water, and the particle scattering is dominated by Rayleigh scattering from the core. As the temperature or salt concentration increases, both the scattering cross-section and the forward scattering increase, characteristic of Mie scatterers. The magnitude of the change in the scattering cross-section and scattering anisotropy can be controlled through the solvent conditions and the size of the core. Such particles may find use as optical switches or optical filters with tunable opacity.

The macroscopic appearance of a colloidal suspension depends strongly on how visible light is scattered from samples. Both the size of the particles and the ratio of refractive indices between particle and solvent medium determine the scattering behavior of a single particle, including magnitude and angular modulation.

Owing to their strong interactions with visible light, colloidal suspensions are used to control the optical properties of a variety of materials, from paints to photonic crystals.[1,2] In principle, it is also possible to synthesize colloidal suspensions with responsive optical properties. Such suspensions could be used as optical switches or tunable filters. There are two ways to tune the scattering properties from a colloidal suspension: one can change how individual particles scatter light, or one can change the structural organization of the particles on the scale of wavelength. Most recent work has focused on the second approach, which has led to many new materials with responsive optical properties. These include colloidal crystals with tunable Bragg diffraction,[3] colloidal "photonic liquids",[4,5] DNA-linked nanoparticle aggregates with variable plasmonic resonances,[6–8] and polymer-dispersed liquid crystals[9] with electrically tunable turbidity. But relatively little work has been done on dynamically controlling the scattering properties of individual particles in a dilute, liquid suspension.

In order to make individual colloidal particles that exhibit responsive scattering properties, the particles must be made of a responsive material. Poly(*N*-isopropylacrylamide) (PNIPAM) is one of the most frequently used polymers in the study of thermoresponsive transitions.[10–12] Several works have focused on the physico-chemical properties of core–shell PS–PNIPAM colloids. The role of a thin PNIPAM shell (<200 nm) in colloidal interactions was described.[13] Optical modifications induced by the PNIPAM transition process have been studied using turbidity measurements and light scattering in concentrated colloidal suspensions.[14–17] However, there are only a few studies showing that the scattering can be designed as a function of temperature.

In this communication, we consider the problem of designing a suspension in which the two fundamental scattering parameters, the scattering cross-section σ_{sc} and scattering anisotropy g,[18,19] can be designed to change with temperature, and where the change can be quantitatively controlled. In previous work, we showed that core–shell particles with large PNIPAM-*co*-AAc shells and small PS cores can be synthesized with prescribed scattering cross-sections.[20] Here, we extend this concept to preparing materials with prescribed responses in terms of both scattering cross-section and scattering anisotropy. We do this by making core–shell particles in which the shell is composed of a thermo-responsive polymer, poly(*N*′-isopropylacrylamide-*co*-acrylic acid) (PNIPAM-*co*-AAc), and the core is a high refractive index polymer, polystyrene (PS). Similar kinds of core–shell particles – and their responsive phoretic[21] and diffusive[22] properties – have been studied by Ballauff and colleagues using light scattering and microscopy.[23,24]

The core–shell approach allows the design of particles that scatter in a qualitatively different way than do homogeneous

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hydrogel particles. Large pure hydrogel particles do not scatter isotropically under any conditions. Although the cross-section changes across the lower critical solution temperature (LCST), the particles are always comparable in size to the wavelength of visible light. They scatter light anisotropically regardless of temperature.

In our approach, the embedded PS core particles scatter light isotropically and have a larger scattering cross-section than the shells, allowing isotropic scattering to dominate over the weak anisotropic scattering of the shell. The key is to synthesize a large (micrometer-scale) and sparse hydrogel shell. At low temperatures, the shell scatters weakly because it is sparse and swollen with water, and its refractive index is nearly matched with that of the aqueous solvent. But the shell is large enough to contain a significant mass of polymer, so that at high temperature it can collapse to form a dense particle comparable in size to the optical wavelength – a Mie scatterer. This approach maximizes the change in optical properties. Moreover, by changing the size of the core in the synthesis, the onset and magnitude of the increase in Mie scattering can be precisely controlled. We find that for these particles σ_{SC} and g change dramatically over a small temperature range. The sharpness of the transition can be varied from about 1 °C to more than 10 °C by changing solvent conditions. Also, the magnitudes of the changes in both scattering parameters, σ_{sc} and g, can be quantitatively controlled by changing the size of the PS core. The resulting core–shell particles can display new types of optical transitions.

First, we demonstrate how the macroscopic appearance of our suspensions changes dramatically when the temperature crosses the LCST of the PNIPAM-*co*-AAc hydrogel shell (Fig. 1). At 22 °C, the core–shell suspensions appear transparent or translucent, and the incident collimated laser beam propagates through the samples with limited scattering. At 35 °C, the suspensions appear opaque and white. Light propagates diffusively, and the incident laser beam loses its original direction and intensity.

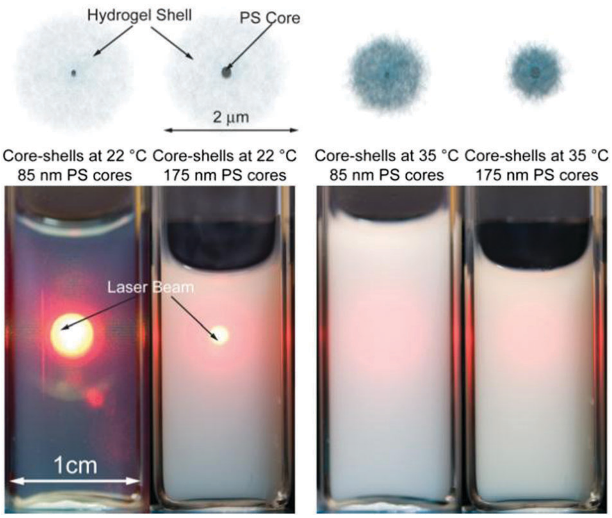

Fig. 1 Macroscopic pictures and schematic diagrams of PS-(PNIPAM-*co*-AAc) core–shell particles suspended in DI water when the shells are swollen at 22 °C and de-swelled at 35 °C. The vials are all 4 mm thick and have the same number density (1.4×10^{15} L^{-1}) of core–shell colloidal particles. Cores are 85 nm and 175 nm diameter PS. The incident laser intensity, background illumination and camera exposure conditions are the same for all pictures.

The change in optical appearance occurs over a surprisingly small temperature range. Using light scattering and turbidimetry, we measure the average change in σ_{SC} for a particle (see Fig. 2). We find that the scattering cross-section σ_{SC}, and therefore the amount of light scattered, changes by a factor of 10 over a narrow temperature range (1.0 °C near 34 °C). The sharpness of this transition is unexpected. As shown in Fig. 2A, the scattering changes much more suddenly than the particle diameter. Although the particle diameter decreases almost 80% between 25 °C and 33 °C, the cross-section remains constant and equal to that of the PS cores alone over the same temperature range. This result suggests that the sparse outer polymeric brush of the hydrogel shell collapses first, changing the hydrodynamic diameter of the particles but not significantly affecting the average segment density of the shell. The partially collapsed hydrogel shells therefore remain optically transparent. As we approach the LCST, the whole crosslinked hydrogel shell appears to shrink, increasing its segment density and refractive index. The schematic diagrams in Fig. 1 illustrate this process. The end result is that the particles behave like optical switches near the LCST.

Both the magnitude and sharpness of the scattering transition can be controlled. The magnitude of the change in scattering cross-section can be controlled by varying the size of the PS cores. Increasing the core size increases the cross-section at low temperature, allowing us to decrease the change in cross-section upon crossing the LCST. As shown in Fig. 2B, core–shell particles with 175 nm PS cores have larger scattering cross-sections at lower temperatures than core–shell particles with 85 nm PS cores; also, they show a smaller change in the scattering cross-section across the LCST than do particles with 85 nm PS cores. The sharpness of the scattering transition can be controlled by solvent parameters such as ionic strength.[25] The dashed lines in Fig. 2A and B show the temperature dependence of the particle size and turbidity of core–shell particles with 85 nm PS cores suspended in 0.5 M NaCl. The excess ions shift the LCST to a lower temperature because they screen the Coulomb repulsive interactions between AAc groups in the hydrogel shell.[26,27] Between 27.5 °C and 33 °C, the average segment density of the hydrogel shell gradually changes, along with the particle size. The scattering cross-section still increases by more than an order of magnitude across the LCST, but the transition is more gradual with temperature.

The particles also show a sudden change in angular scattering anisotropy across the LCST. Fig. 2C shows static angular light scattering measurements from core–shells with 175 nm PS cores in DI water. At 25 °C, the angular scattering of the core–shell particles is weak and nearly isotropic, which are features of Rayleigh scattering.

The angular pattern matches that of pure PS core particles precisely, both in magnitude and in angular dependence. Thus, the scattering behavior is determined entirely by the 175 nm PS core; the micron sized hydrogel shell is transparent and does

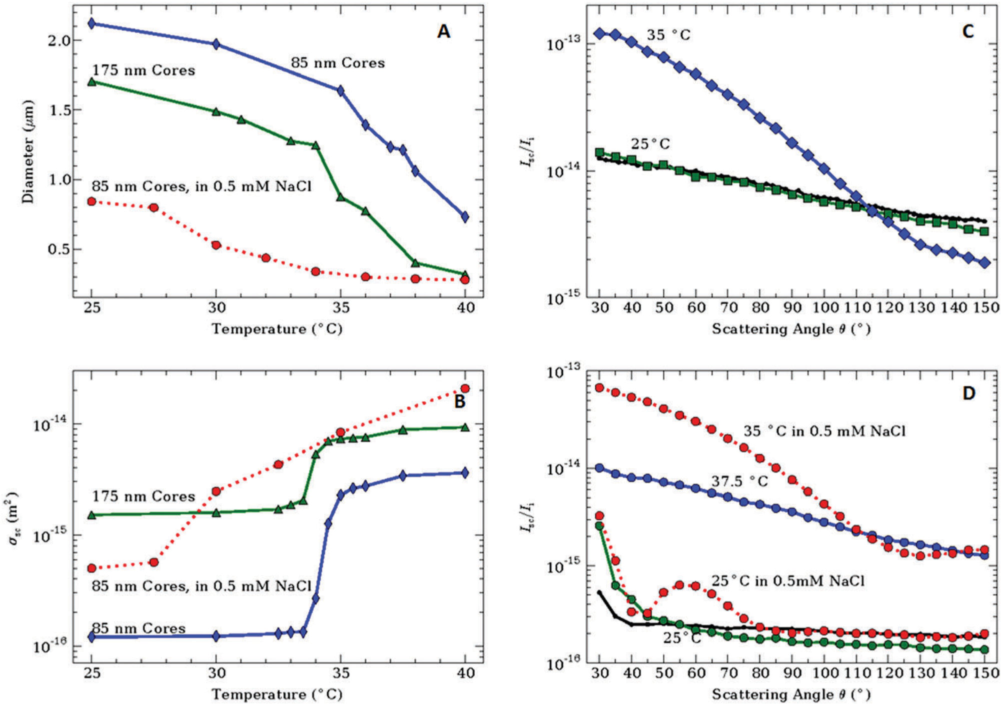

Fig. 2 Temperature dependence of the (A) particle diameter and (B) total scattering cross-section σ_{sc} of PS–(PNIPAM-*co*-AAc) core–shell particles with different core sizes, 85 nm and 175 nm. (C) Static angular light scattering of PS–(PNIPAM-*co*-AAc) core–shell particles with 175 nm cores in DI water at different temperatures. The values are normalized to particle number density in the solutions. The black dots show the scattering from pure 175 nm PS cores. (D) Static angular light scattering of PS–(PNIPAM-*co*-AAc) core–shell particles with 85 nm cores under different solvent conditions. The values are normalized to particle number density in the solutions. The black dots show the scattering from pure 85 nm PS cores. The red dotted lines show the scattering of core–shell particles in 0.5 mM NaCl at different temperatures.

not contribute to the scattering. At 35 °C (above the LCST), the forward scattering ($\theta < 40°$) increases by an order of magnitude. The strong anisotropy is characteristic of Mie scattering. A similar transition can be seen with core–shell particles with 85 nm PS cores in DI water, which change from Rayleigh scattering at 25 °C to Mie scattering at 37.5 °C, as shown in Fig. 2D.

Therefore we conclude that these core–shell particles exhibit a Rayleigh-to-Mie scattering transition. The angular scattering behaviors of our core–shell particles are responsive to both temperature and ionic strength in the solvent. In the presence of 0.5 M NaCl, the scattering from the core–shell particles is anisotropic at 25 °C, and it becomes much more so at 35 °C, compared to the scattering in DI water at 37.5 °C.

The Rayleigh-to-Mie transition manifests itself in how light diffuses through the sample. Although both 175 nm core samples in Fig. 1 look white, the light that propagates through the high-temperature sample is multiply scattered over a broader range of angles. The degree to which the direction of light is randomized is quantified by the transport mean free path l_{tr}, which is a function of the anisotropy parameter g. We measure this parameter by diffuse-transmission spectroscopy.[28] Table 1 summarizes the g values measured for core–shell particles with different PS core sizes above and below the LCST. At 25 °C, g is close to zero, the Rayleigh scattering case. Again, the scattering is dominated by small PS cores. At 37.5 °C, g is close to 1, the Mie scattering case. g is comparable for both core/shell particles with 85 nm cores and core/shell particles with 175 nm cores, indicating that it is primarily the collapsed hydrogel shell that dominates the scattering at high temperature.

Table 1 Scattering anisotropy parameter g of core–shell particles at different temperatures

Sample	25 °C	37.5 °C
Core–shells with 85 nm cores	0.051[a]	0.715
Core–shells with 175 nm cores	0.211[b]	0.837

[a] Calculated value. [b] Measured value for PS core particles.

Conclusions

We have therefore demonstrated that the macroscopic appearance and transport of light through this core–shell colloidal suspension can be actively controlled. Both the scattering cross-section and anisotropy can be characterized and dynamically controlled *in situ* by changing temperature or solvent conditions. The magnitude of the response can be controlled during the chemical synthesis by varying the sizes of the PS core and the hydrogel shell. The variation with temperature can be changed from gradual to sharp by varying the ionic strength in the solvent. This type of dynamic colloidal suspension may prove useful in devices where scattering needs to be well controlled, such as information displays[5,29] and optical filters. Because the anisotropy is related to the distance over which the direction of light becomes randomized, such particles may also prove useful in privacy filters. Future work might combine this approach with control over the spatial correlations between particles, leading to applications in devices such as random lasers.[30]

Conflicts of interest

There are no conflicts to declare.

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