Multiphasic Nanocolloids Based on Electrified Co-Jetting

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INTRODUCTION

One of the major challenges in current nanotechnology is the control of materials distribution at ultra-small length scales, potentially leading to the fabrication of multi-wavelength nanoparticles. One of the simplest versions thereof are two-sided particles, so called Janus particles, which are believed to be of importance for designing active nanostructures or as functional elements in future device generations. In recent years, various methods have been developed to fabricate Janus particles including surface modification with partial masking, selective deposition, microcontact printing, template-assisted self-assembly, emulsion polymerization, surface nucleation, or the modification of core-shell particles. Most of these approaches are intrinsically limited to binary systems making the fabrication of multi-compartmental nanoparticles an exceptional challenge.

EXPERIMENTALS

Materials. PEO, PAA, FITC-dextran (MW 250 kD), rhodamine-B-dextran (MW 70 kD) and Atto655-NHS-ester dye were purchased from Aldrich, Inc., USA. PAAm-co-AA (MW 200 kD) was purchased from Polysciences, Inc., USA. Alexa Fluor® 647-conjugated bovine serum album (BSA) (MW 66 kD) and amino-dextran (MW 70 kD) were purchased from Molecular Probes, Inc., USA.

Solution Preparation. To purify the PEO solutions, centrifugation and filtration were performed prior to use. The other solutions were used without further purification. Every solution was prepared by mixing all components (as well as with distilled water, reported as percentage of weight per volume). Every fluorescent dye-conjugated biomolecule except Atto 655-conjugated dextran was used as purchased. Atto 655-dextran was prepared by 2 hour reaction between 50 mg of amino dextran and 0.35 mg of Atto 655-NHS-ester dye in 5 ml of distilled water followed by membrane dialysis and lyophilization. Detailed composition of jetting polymer solutions are summarized in Table 1S.

Electrified Co-Jetting. Each of three jetting solution was stored in a 1 ml plastic syringe (Becton, Dickinson and Company, NJ, USA). The flow rate was controlled by a syringe pump (KDS100, KD Scientific Inc., MA, USA) in the range of μl min⁻¹. The flow rate was controlled by a syringe pump (KDS100, KD Scientific Inc., MA, USA) in the range of μl min⁻¹. Three parallel capillaries were assembled by putting three conducting needles (20 gauges, 5 cm long) as described in the main text. A transparent plastic tube was used to encircle the capillaries together. Positive voltage was applied with high potential generator (ES30P, Gamma High Voltage Research, Inc., USA). Detailed working parameters for different polymer solutions and the resulting morphologies are summarized in Table 1S.

Thermal Imidization. Thermal imidization were performed at 175 °C for 3 hours in a convection oven before the stabilized nanocolloids were suspended in water. When necessary, 5 minutes of tip-type sonication was performed to prepare well suspended nanocolloids.

Confocal Laser Scanning Microscopy. Images were taken with a SP2 CLSM (Leica, USA). Each fluorescent dye was excited with different lasers (Ar/Kr laser at 488 nm for FITC, Green laser at 543 nm for Rhodamine B and HeNe laser at 633 nm for Alexa Fluor® 647 or Atto 655). Individual phases were observed in separate windows for their characteristic emission wavelength ranges (505-535 nm for FITC, 570-610 nm for Rhodamine B and 655-700 nm for Alexa Fluor® 647 or Atto 655). For a better phase distinction, the colors for each observation channel were digitally designated differently from the actual emission colors (blue, green and red for FITC, Rhodamine and Alexa Fluor 647 or Atto 655 respectively).

RESULTS AND DISCUSSION

The fabrication of multi-phasic nanocolloids, can be achieved by using an approach based on of electrified co-jetting as an alternative approach towards Janus-type nanocolloids. The electrified co-jetting process exploits the manipulation of liquid jets with nano-meter scale diameters created under the influence of electrohydrodynamic forces. It also can be extended the concept of electrified co-jetting to the simultaneous manipulation of three liquid flows; thereby establishing a versatile and simple avenue towards triphasic nanocolloids, i.e. nanocolloids with three distinct compartments.

In our co-jetting experiments, a laminar flow of three distinct polymer solutions was pumped at suitable flow rates, typically in the range of μl min⁻¹, through a modified nozzle with side-by-side geometry. The capillaries are aligned to form a triangular cross-sectional geometry. Because the laminar flow regime extends through the needles into the outlet region, droplets with three distinct interfaces can be formed. Once the triphasic nanocolloids were prepared, we used confocal laser scanning microscopy (CLSM) and scanning electron microscopy (SEM) for characterization.

The use of aqueous solutions for electrified co-jetting leads to nanocolloids that are inevitably water-soluble. Studying triphasic nanocolloids in aqueous environments will therefore require an extra modification step to stabilize the nanocolloids. The stabilization of polymer-based micro/nano structures has been achieved by photochemical or thermal crosslinking. To stabilize the triphasic nanocolloids, we turned to the thermal imidazolation, i.e., the temperature-induced crosslinking of carboxylic acid groups of PAA with amide groups of PAAm. We recently showed that thermal imidazolation becomes an effective way to stabilize the PAA- and PAAm-based nanocolloids.

To probe the aqueous stability of triphasic nanoparticles crosslinked by thermal imidazolation, we incorporated differently colored biomacromolecular dyes into the aqueous solutions of poly(acrylamide-co-acrylic acid, sodium salt) (MW 200 kD, 10% acrylic acid residues) and polyacrylic acid (MW 250 kD). After co-jetting and subsequent thermal crosslinking at 175°C for 3 hours, the nanocolloids were suspended in water and imaged by CLSM.

Figure 1. Triphasic nanoparticles after electrified co-jetting, thermal crosslinking and storage water for 1 week.

CONCLUSIONS

In summary, we have shown that macro-scale fluid manipulation can be utilized for the fabrication of anisotropic nanoparticles with multiple compartmentalization. The fact that these novel nanocolloids are fabricated by electrified co-jetting suggests that the proposed technology may be broadly applicable to a wide range of different polymers and polymer composites. Nevertheless, more complete understanding of multi-component nano-objects will need to be developed, before the exciting potential of triphasic nanocolloids in self-assembly processes or for the development of novel imaging probes can be evaluated. Once these technological hurdles are overcome, multiphasic nanoparticles, such as the triphasic nanocolloids of this study, could be of great interest for applications in the fields of drug delivery, molecular imaging, and smart displays.
REFERENCES