ANISOTROPIC ENCAPSULATION OF SUPERPARAMAGNETIC NANOCRYSTALS IN POLYMERIC BIPHASIC NANOCOLLOIDS

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Introduction

Electrostatic jetting has been widely used to create nanofibers of polymer-nanoparticle composites.\(^1\) Especially, magnetic nanofibers have been produced by incorporation of iron oxide nanoparticles.\(^{2-4}\) In these previous composite structures, the nanocrystals are randomly or homogeneously encapsulated.

We recently have shown that anisotropic material distribution in nano-objects can be achieved by electrified co-jetting of multiple jetting solutions in side-by-side geometry.\(^5,6\) In the current study, we intend to show that this process is also applicable to fabricate anisotropic polymer-nanocrystal composite geometry. With an intention to induce directional functionality, superparamagnetic iron oxide nanocrystals were encapsulated selectively in one hemisphere of a polymeric nanocolloid by use of side-by-side electrified co-jetting. Magnetite (Fe\(_3\)O\(_4\)) nanocrystals with diameters of 5 to 20 nm were synthesized by co-precipitation of ferrous and ferric ions in the presence of polyacrylic acid. For the jetting, either poly(acrylamide-co-acrylic acid) or polyacrylic acid was dissolved into the aqueous suspension of magnetite nanocrystals. For the side-by-side dual jetting geometry, the nanocrystal suspension mixed with a polymer solution was used as a jetting solution for one side in parallel with a corresponding empty polymer solution in the other side simultaneously. Transmission electron microscopy was employed to characterize the biphasic nature of the resulting nanocolloids. These magnetic nanocolloids with unique anisotropy can be useful for novel display device, magnetically controlled biomedical imaging or targeted drug delivery.

Experimental

Materials. Ferric chloride hexahydrate (FeCl\(_3\)·6H\(_2\)O), ferrous chloride tetrahydrate (FeCl\(_2\)·4H\(_2\)O), poly(acrylic acid) (PAA, MW 250k), FITC-dextran (MW 70k) and rhodamine B-dextran (MW 70k) were purchased from Sigma-Aldrich, Inc. USA. Poly(acrylamide-co-acrylic acid) (PAAm-co-AA, MW 200k, 10% acrylic acid residues) was purchased from Polysciences, Inc. USA. All reagents were used without further purification.

Synthesis of Magnetite Nanocrystal. Magnetite nanocrystals were synthesized by a modified method of two previous reports.\(^6,7\) First, mixed aqueous solutions of ferrous chloride (0.1M), ferric chloride (0.2M) and PAA (1%, w/v) were prepared by stirring while purging with Ar gas. After 30 minutes of stirring, the pH of the solution was increased to above 10 by adding 0.1 M NaOH solution. The solution was aged for an hour subsequently, while being kept under inert conditions.

Jetting Solution Preparation. The magnetite nanocrystal suspension was washed with fresh distilled water once after centrifugation, before it was mixed with polymers. PAAm-co-AA or PAA was directly added in the nanocrystal suspensions with the final concentrations of 5% (w/v) and 10% (w/v) respectively, and dissolved by continuous stirring and a subsequent sonication step. An aqueous solution of each polymer of the same concentration with the nanocrystals was prepared and used for the other side of the jetting solution. 0.5% (w/v) of rhodamine B-dextran and 0.5% (w/v) of FITC-dextran were added to the jetting solutions with and without the nanocrystals, respectively.

Side-by-Side Electrified Co-Jetting. We followed the same method of our previous reports on the electrified co-jetting.\(^1,2\) Two syringes loaded with a specific jetting solution were set up side-by-side and the flow rate was controlled by a single syringe pump. A dual channel tip (FibriJet® SA-0105, Micromedics, Inc., MN, USA) was connected to the two syringes. Positive voltage was applied with a high potential generator (ES30P, Gamma High Voltage Research, Inc., USA) between the dual capillaries and a piece of aluminum foil (about 10 square inches) as a collecting substrate.

Characterization. JEOL 2010F was operated at the accelerating voltage of 200 kV for transmission electron microscopy. The nanocolloids were directly jetted on top of a carbon-coated copper grid (Ted Pella, Inc. USA). SP2 CLSM (Leica, USA) was used for confocal microscopy. Ar/ArKr laser at 488 nm and GreNe laser at 543 nm were used to excite FITC and rhodamine B, respectively. The characteristic emission signals for the dyes were collected in separate wavelength windows.

Results and Discussion

Side-by-Side Electrified Co-Jetting. Figure 1 shows the scheme of experimental setup of the electrified co-jetting process and the resulting nanocolloids. The polymer solutions with and without the magnetite nanocrystals suspended were pumped throughout the nozzles with side-by-side geometry. When high electrical voltage was applied to the pendant droplet, a thin liquid jet was ejected from the interface between the two jetting solutions. If the anisotropic distribution of the nanocrystals is preserved until the jet is disintegrated with simultaneous drying, the resulting nanocolloids would also possess nanocrystals selectively in one hemisphere.

Figure 1. Schematic description of electrified co-jetting process and a cartoon showing the geometry of the resulting nanocolloids.

Figure 2 shows typical examples of TEM images of the resulting nanocolloids. As intended, the nanocrystals are encapsulated not randomly or homogeneously but anisotropically inside of polymeric nanocolloids with diameters of several hundred nanometers. This was true for both nanocolloids made of PAAm-co-AA and PAA. However, it is worthy to note that not every particle in TEM images showed this anisotropic geometry. And the volume fraction of empty phase in a particular particle was not always identical to those of others. This might be attributed either to the 2-dimensional character of TEM images or to the imperfect co-jetting behavior.

These nanocolloids would be very useful if dyes or drugs could also be also loaded in biphasic manner. In order to test this, dextran molecules conjugated with two fluorescent dyes were incorporated in each side of jetting solutions. The resulting nanocolloids were suspended in immersion oil (Leica, USA) and...
examined by confocal microscopy (Figure 3). The overlay image of emission signals from the two dyes confirms that the nanocolloids are color-coded, also in an anisotropic manner.

**Figure 3.** Confocal laser scanning microscope image of magnetic nanocolloids suspended in immersion oil. Rhodamine B-dextran (red) was originally incorporated in the jetting solution with the magnetite nanocrystals and FITC-dextran (green) in the empty polymer solution side.

**Conclusions**

Electrified co-jetting was successfully utilized to produce polymeric nanocolloids containing magnetic nanocrystals in anisotropic geometry. This research shows that anisotropic encapsulation of various functional nanomaterials inside of polymeric colloids is possible by a well-designed electrified co-jetting process. The nanocolloids based on PAAm-co-AA in this study can further be crosslinked by simple thermal treatment. Considering that various dyes or drugs can also be loaded in each phase, these magnetic nanocolloids with novel geometry can be useful for display device, magnetically controlled biomedical imaging or targeted drug delivery. Detailed characterization and the application study of these nanocolloids are currently ongoing.

**References**