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Fabrication of "Hairy" Colloidosomes with Shells of Polymeric Microrods

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Colloidosomes are microcapsules whose shells consist of coagulated or fused colloid particles.[1−6] Such microcapsules offer a great potential in controlling the permeability of entrapped species by varying the particle size and their degree of fusing and may find various applications in pharmaceutical, cosmetic, and food industries. Velev et al.[1] were the first to report a method for preparation of colloidosomes by templating octanol-in-water emulsions stabilized by latex particles and by subsequently removing the oil core by dissolution in ethanol. Similar structures have also been obtained by templating water-in-oil emulsions.[2,3] Wang and Caruso[4] and Kumaraswamy et al.[5] have used layer-by-layer assembly of multilayer shells consisting of alternating cationic and anionic polyelectrolytes and/or nanoparticles. The final hollow shells are obtained by removal of the central, sacrificial colloidal particles. Dinsmore et al.[6] have produced colloidosomes by assembly of latex particles into shells around water-in-oil emulsion drops followed by partial fusion of the shell and centrifugal transfer into water.

Here, we report fabrication of novel colloidosome microcapsules with a shell of polymeric microrods. The basics of the method are illustrated in Figure 1. The synthesis involves three stages: (i) Hot aqueous solution of agarose is emulsified in oil in the presence of rodlike polymeric particles to produce a stable water-in-oil emulsion stabilized by the solid particles, and the system is cooled off to set the agarose gel. (ii) The obtained suspension of aqueous gel microcapsules is diluted with ethanol and centrifuged to separate them from the supernatant. (iii) The microcapsules are washed with ethanol and water and redispersed into water. This technique allows preparation of colloidosome microcapsules of diameters varying between several tens to several hundreds of micrometers. The function of the gel cores is to support the particle shell and to give the microcapsules enough stiffness to be separated from the oil phase by centrifugation. Details of the method are given below.

Tricaprylin (min 99%, from Sigma) was used as an oil phase without further purification. Agarose (D5) was supplied from Hispanagar (Spain). Polymeric microrods were prepared from SU-8 25 photoresist epoxy resin (MicroChem, U.S.A.) by liquid−liquid dispersion of γ-butyrolactone (GBL) solution of the resin in mixture of glycerol and ethylene glycol (Fisher Scientific, U.S.A.) at constant shear as described by us elsewhere.[7] After the synthesis, the rodlike particles were further strengthened by cross-linking with UV light (365 nm), transferred to water, and concentrated by multiple washing/centrifugation cycles. The microrod sample was characterized by optical microscopy and scanning electron microscopy (SEM). It was found out that it consists of polydisperse rods with lengths in the region 10−70 μm and diameters of 0.4−2.0 μm. Figure 2A represents a typical optical microscope image of a suspension of the polymeric microrods in water. We used the recently developed gel trapping technique (GTT)[8] to determine the wettability of the individual epoxy microrods at the tricaprylin−water interface. Twenty microliters of a 50:50 mixture of the microrods suspension and 2-propanol was spread at the interface between tricaprylin and hot agarose solution. After cooling off and setting the gel (1.5% agarose in water), the top phase was replaced with curable poly(dimethylsiloxane) (PDMS, Sylgard 184 from Dow Corning). After cross-linking, the solidified PDMS was peeled off the gel, and the microrods trapped at the PDMS surface were imaged with SEM to reveal their position with respect to the original liquid interface. Figure 2B shows a microrod picked up with PDMS from the tricaprylin−water interface. These experiments allowed us to estimate the wettability of the microrods at the interface between the oil and the agarose solution. The contact angle of the rods adsorbed at the tricaprylin−water surface is larger than 90°. This indicates that the microrods are very hydrophobic and are more likely to stabilize water-in-oil emulsions.

The aqueous suspension of SU-8 microrods was concentrated to 6.2 wt % solid content, and 300 μL of it was added to 7.5 mg agarose and toped up to 500 μL with milliQ water. The agarose

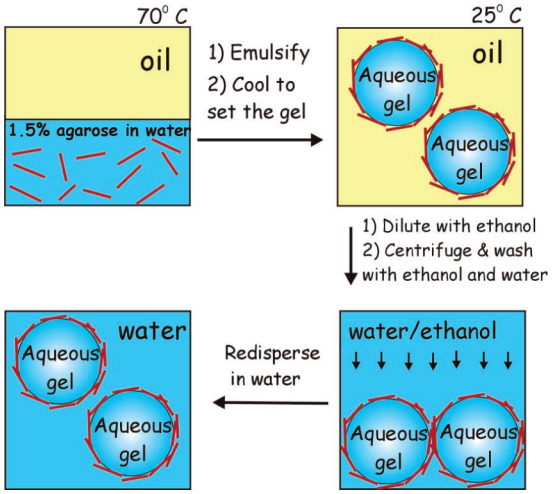

Figure 1. Schematics of the method for preparation of the gelled colloidosomes of polymeric microrods.

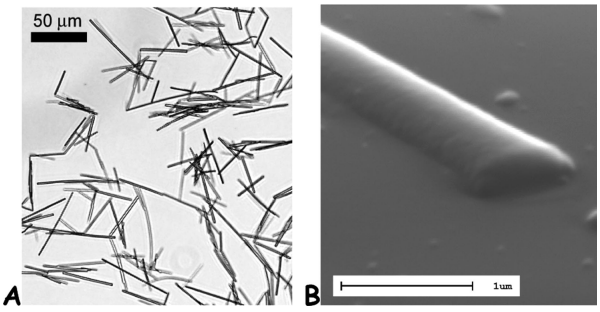

Figure 2. (A) Optical micrograph of the SU-8 microrod particles dispersed in water. (B) SEM image of a single SU-8 microrod partially embedded on PDMS after being picked up from the oil−water surface with the GTT.[8] The visible part of the microrod has initially been in contact with the aqueous phase, while the part embedded in the PDMS has been in contact with the oil.

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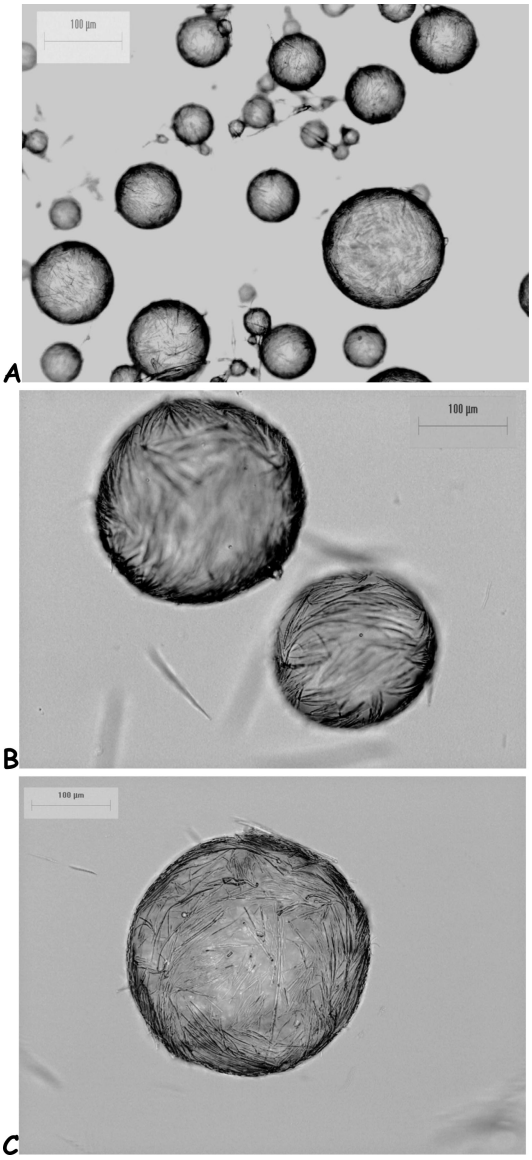

Figure 3. (A) Hot water-in-tricaprylin emulsion stabilized solely by SU-8 microrods. (B) Agarose gel beads coated with polymeric microrods in tricaprylin obtained by gelling of the emulsion. (C) "Hairy" colloidosome microcapsules produced by transferring the microrod-coated agarose beads in water.

was dissolved by heating to 95 °C, and then the solution was mixed with 4.5 mL of tricaprylin, emulsified by multiple passing (six times) through a preheated syringe with a needle of diameter 0.8 mm and kept at 70 °C. A sample of the hot emulsion was visualized on a preheated microscope slide by optical microscopy. Figure 3a shows a typical image of the water drops in tricaprylin which appear to be fully coated with microrods adsorbed at the oil−water interface. Note that the emulsion is stabilized only by the adsorbed hydrophobic microrods, which indicates that such particles have a great potential as emulsifying agents. Due to the dense layer of adsorbed microrods the coalescence between the drops of emulsified hot agarose solution stops completely. The stabilizing effect of the microrod particles is likely to come from sterical obstruction of the interdrop contacts by partially adsorbed microrods. While the same factors are the basis of emulsion stabilization by any solid particles, we believe that the microrods studied here may have specific advantages in making stable and coherent shells.

For the preparation of colloidosome capsules, the hot water-in-tricaprylin emulsion stabilized by the polymeric microrods was cooled to room temperature to set the agarose gel. Figure 3B shows a typical image of the aqueous gel capsules coated with shells of microrods in tricaprylin. It was found that the gelling of the aqueous cores strengthens the shell of microrod particles at the capsule surface. This allowed the separation of the capsules from the tricaprylin phase without considerable loss of adsorbed particles. The latter was done by 10-fold dilution of the emulsion with ethanol and multiple centrifugations of the capsules, followed by washing with ethanol and water. The colloidosome capsules were then transferred in water and imaged by optical microscopy. We also succeeded in further improving the retention of microrods on the surface of the colloidosomes by cross-linking them in the shell with glutaraldehyde. For this purpose, 1 mL of glutaraldehyde solution (70% in water) was stirred with 1 mL of tricaprylin for 2 h. Twenty microliters of the tricaprylin phase saturated with glutaraldehyde was added to the water-in-oil emulsion, and the system was stirred for 2 h before dilution with ethanol and centrifugation as described above. Figure 3C shows an optical image of the obtained "hairy" colloidosome capsules redispersed in water after their shells have been strengthened by glutaraldehyde cross-linking.

The agarose gel core is essential for the structural integrity of our colloidosome microcapsules. The gel core gives the capsules enough mechanical strength to survive the treatment with ethanol, the centrifugation/washing cycles, and the transfer in water and preserves the structure of the colloidosome membrane. In addition, the presence of an agarose gel in the core of the colloidosome capsules provides the advantage of two levels of encapsulation. The first level is provided by the gel network through which pore size is determined by the agarose concentration. The second level is the colloidosome membrane which determines the total out-flux of released component from the capsule. The pore size of the membrane controls the permeability of the colloidosome that allows more degrees of freedom for tuning the release kinetics of entrapped components.[6]

In summary, we report the first preparation of: (a) emulsions stabilized solely by microrods (microfibers) and (b) "hairy" colloidosomes whose shells consist of microrod particles. We have designed and fabricated novel colloidosome capsules that consist of aqueous gel cores and shells of polymeric microrods. This has been achieved by templating water-in-oil emulsions stabilized by rodlike particles followed by gelling of the aqueous phase, dissolution of the oil phase in ethanol, and redispersion of the obtained colloidosome microcapsules in water. The microrod shell around the colloidosomes may impart superior mechanical stability compared to the previously used microspheres.[1−2] Such capsules may find applications as delivery vehicles and for controlled release of drugs, cosmetics, and food supplements.

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Supporting Information Available: Experimental details for preparation and properties of the microrods used. This material is available free of charge via Internet at http://pubs.acs.org.

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