Supporting Information for:

Formation of Hybrid Core-Shell Microgels Induced By Autonomous Unidirectional Migration of Nanoparticles

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Experimental

Materials: Silver nitrate ($AgNO_3$), cetyltrimethylammonium bromide (CTAB), sodium oleate, hydrochloric acid (HCl), ascorbic acid, chloroauric acid ($HAuCl_4$), sodium borohydride ($NaBH_4$), calcium iodide (CaI_2), ammonium hydroxide ($NH_3 \cdot H_2O$), iron (II) chloride ($FeCl_2 \cdot 4H_2O$), iron(III) chloride ($FeCl_3 \cdot 6H_2O$), CdSe QDs, sulfur powder, dodecanethiol (DDT), stearic acid (SA), octadecylamine (OAm), 1-octadecene (ODE), 11-mercaptoundecanoic acid (MUA), rhodamine B isothiocyanate (Rh B), (3-aminopropyl)triethoxysilane (APTS), and tetramethylammonium hydroxide (TMAH), trichloro (1H,1H,2H,2H-perfluorooctyl) silane (TPFS), tetraethyl orthosilicate (TEOS), ethanol, poly(vinyl alcohol) (PVA, M_w=13,000-23,000, 87-89 % hydrolyzed), I-carrageenan, sodium carboxymethylcellulose and 1-undecanol were purchased from Sigma-Aldrich. Calcium Carbonate ($CaCO_3$) nanoparticles (NPs) with a diameter of ~30-40 nm were purchased from Skyspring Nanometrials, Inc. Sodium alginate (Manucol®LKX) was kindly provided by FMC biopolymer company. All reagents were utilized as received. Ultrapure water was used to prepare all the aqueous solutions.

Fabrication of microfluidic devices: Monodisperse emulsion droplets were prepared using a co-flow microcapillary device. Briefly, one round glass capillary (World Precision Instruments) with outer and inner diameters of 1.0 mm and 580 μm was firstly tapered to achieve an orifice of ~ 60-100 μm by using a micropipette puller (Narishige PC-10) and a microforge (Narishige MF-900). The tapered round capillary was used for introducing the fluid of dispersed phase into the microfluidic device. The tapered round capillary and another non-tapered round capillary (as a collection tube) were then assembled into the square capillary with an inner diameter of 1.0 mm. The tip of the tapered round capillary was inserted into the collection tube. The position of the two tubes were adjusted to maintain a suitable distance in-between, in order to allow the fluid of continuous phase to flow in the collection tube. Subsequently, a transparent epoxy resin was used to seal the tubes, if needed. To ensure the stable generation of monodisperse water-in-oil emulsion droplets, the inner wall of the collection tube was treated with TPFS to achieve a hydrophobic surface.

Synthesis of gold NPs and gold nanorods (NRs): Au NPs were synthesized according to a previously reported approach with some modifications.[1] Briefly, 10 mg of $HAuCl_4$ was first dissoved into 500 mL of water. After boiling the above solution, 3 mL of aqueous solution containing 1 wt % sodium citrate was injected into the above boiling solution. Then, after decreasing the temperature to 85 ºC and the solution turned light red; another 3 mL of aqueous solution containing 1 wt % sodium citrate was added quickly, followed by the addition of 1 mL solution of $HAuCl_4$ with concentration of 10 mg/mL. The above step was repeated six times for every 15 min. After that, the mixture containing Au NPs was cooled down to the room temperature, which was ready for further use without purification.

Au NRs were synthesized according to a previously reported method with some modifications.[2] The synthesis can be separated into two steps: the seed solution and the growth solution. In brief, the seed solution was prepared by injecting 600 μL of 0.01M $NaBH_4$ into a 10 mL solution of 0.1 M CTAB and 2.5×10^{-4} M $HAuCl_4$ under vigorously stirring, followed by keeping at 30 ºC for ~ 30 min before use. For the growth solution, 4.20 g of CTAB and 0.7404 g of sodium oleate were dissolved in 150 mL water (solution 1) in a 500 mL erlenmeyer flask under heating. After cooling down to room temperature, solution 1 was set in a water bath of 30 ºC while adding 10.8 mL of 4 mM $AgNO_3$ solution. 15 min later, another 150 mL aqueous solution containing 0.0591 g $HAuCl_4$ was quickly added to solution 1 with stirring at 700 rpm. After 90 minutes, 900 μL HCl (37 %) was injected into the solution under stirring at 400 rpm. Another 15 min later, 240 μL seed solution and 750 μL of 0.064 M ascorbic acid were added to the above solution. The solution was taken off the stir-plate and placed in a 30 ºC water bath overnight. The product was purified and concentrated by two cycles of centrifugation with 5000 rpm for further use.

***Synthesis of Fe_3O_4 NPs*:**[3] Briefly, a certain amount of $FeCl_2\cdot4H_2O$ and $FeCl_3\cdot6H_2O$ were dissolved in a flask with 500 mL H_2O. Then, the above solution was set in a water bath of 30 ºC. A certain amount of $NH_3\cdot H_2O$ was added to the solution with vigorously stirring. After the color of the solution changed from yellow to dark brown, the reaction was performed for 25 min. Then, the samples were washed several times using pure water until the pH value is 7.0. Subsequently, the magnetic Fe_3O_4 NPs obtained were redispersed in water for further use.

***Synthesis of Rh B doped silica NPs*:** Synthesis of the Rh B doped silica NPs was synthesized by using a modified Stöber method.[4] Briefly, a certain amount of Rh B was first dissolved in ethanol and reacted with APTS for 20 h in the dark under stirring. Second, a certain amount of $NH_3\cdot H_2O$ and ethanol were added to the mixture and reacted with stirring for 20 h in the dark. Finally, TEOS was added into the above solution and reacted for another 24 h while continuously stirring. After the reaction, the samples were centrifuged and purified to obtain the Rh B doped silica NPs.

***Preparation of hybrid core-shell hydrogel particles*:** Based on the reported approach on the fabrication of alginate capsules,[5] monodisperse aqueous droplets and the resulting hybrid core-shell microgels were prepared by using a combination of the microfluidic and ionic-crosslinking-induced NP migration technique. The aqueous suspensions containing various inorganic NPs (Au NRs, Au NPs, QDs, silica NPs, $CaCO_3$ and Fe_3O_4 NPs) with different content, sodium alginate (1 wt %), and PVA (1 wt %) were used as inner phase; The mixture of undecanol with different concentration of CaI_2 were used as outer phase. The above two solution flow through the co-flow microfluidic device, forming the monodisperse emulsion droplets. The flow rate of external oil phase and inner aqueous phase could be controlled by the syringe pump, which was usually set at 60 μL/min and 5 μL/min, respectively. The resulting emulsion droplets were collected into the polystyrene (PS) petri dish containing undecanol with CaI_2. For the hybrid hydrogel particles with different shapes, different specific hydrophobic geometry, including hollow cylinders, or hollow hexagonal plates, were chosen. After that, the specific geometry filled with aqueous solution were placed in the oil phase. The oil could easily wet the inner surface and form a thin layer of oil due to the hydrophobic property of the inner surface of the channel. Ca^{2+} ions in the oil phase can be used as crosslinker to crosslink the alginate from the surface to the center of droplets gradually. The core-shell structure were formed during the process of crosslinking. After complete crosslinking, the resulting core-shell hybrid microgels were obtained followed by washing with isopropanol and water. The obtained core-shell hybrid microgels were dispersed in water for further investigation.

Preparation of hybrid core-shell microgels with controlled shapes**:** Plastic tubes (~1-2 mm in diameter and 3-5 mm in length) with cross-sections of different shapes were used for the demonstration of the concept. The tubes with different shapes were filled with aqueous alginate droplets containing different inorganic NPs using micropipettes and placed in a solution of CaI_2 in undecanol. The wetting of the inner surface of the container by undecanol produced a thin layer of oil between the droplet and the surface of the container. This allows the continuous diffusion of Ca^{2+} ions from all the directions into the droplet. The complete gelation of the droplet in ~12 hours generated hybrid core-shell microgels with concentrated NPs in the cores.

Characterizations**:** Microstructures of the core-shell hybrid microgels and inorganic NPs were characterized by a Hitachi SU-70 Schottky field emission gun Scanning Electron Microscope (FEG-SEM) and a JEOL FEG Transmission Electron Microscope (FEG-TEM). Before SEM investigation, the hybrid core-shell microgels and the inorganic NPs were dried in air and coated with a thin layer of Au. TEM samples were prepared by dropping the sample suspension on TEM grid precovered with carbon film, followed by drying at room temperature. Zeta potentials of different solutions containing varied inorganic NPs or polymers were measured by using Zeta potential analyzer (Malvern Instruments Ltd). Optical and fluorescence microscopy images of the core-shell hybrid microgels were monitored by a Nikon Eclipse Ti-S fluorescence microscope equipped with a high-speed camera (exposition time: 1 μs).

References:

[1] G. Frens, *Nature-Phys. Sci*. **1973**, *241*, 20.
[2] X. Ye, C. Zheng, J. Chen, Y. Gao, C. B. Murray, *Nano Lett*. **2013**, *13*, 765.
[3] I. Martínez-Mera, M. E. Espinosa-Pesqueira, R. Pérez-Hernández, J. Arenas-Alatorre, *Mater. Lett*. **2007**, *61*, 4447.
[4] H. Liu, Y. Wang, H. Li, Z. Wang, D. Xu, *Dyes Pigm*. **2013**, *98*, 119.
[5] H. Zhang, E. Tumarkin, R. Peerani, Z. H. Nie, R. M. A. Sullan, G. C. Walker, E. Kumacheva, *J. Am. Chem. Soc.* **2006**, *128*, 12205.

Supporting Figures:

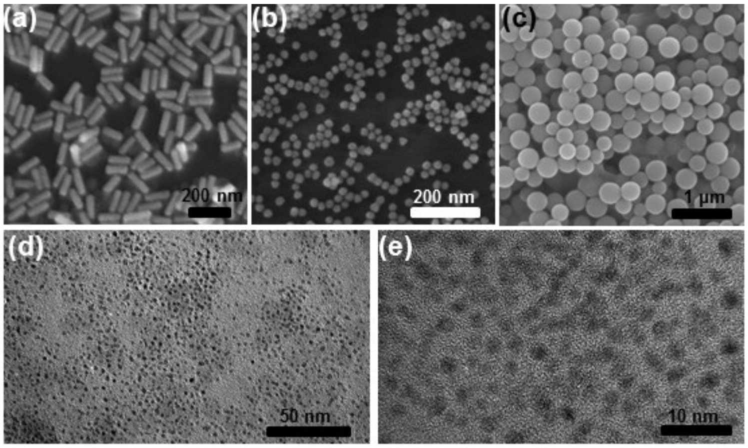

Figure S1. (a-c) SEM images of the Au NRs (a), Au NPs (b), and Rh B doped silica NPs (c), respectively; (d, e) TEM images of the Fe_3O_4 NPs (d), and QDs (e), respectively.

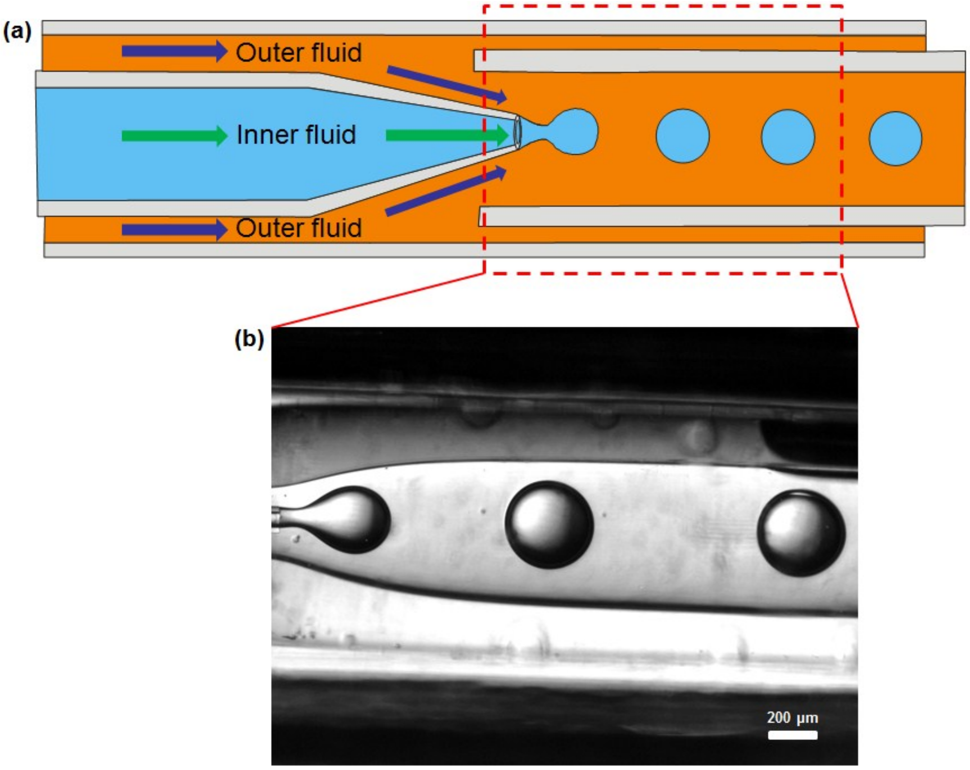

Figure S2. (a) Schematic illustration of the generation of monodisperse water-in-oil droplets using a microfluidic device. An aqueous solution containing sodium alginate, inorganic NPs and poly(vinyl alcohol) (PVA) surfactant was used as the droplet phase, while undecanol was used as the continuous phase. When the two liquids were forced through a narrow orifice, monodispersed droplets were generated in the downstream channel. (b) Optical microscopy image of the formation of monodispersed alginate droplets in the microfluidic channel.

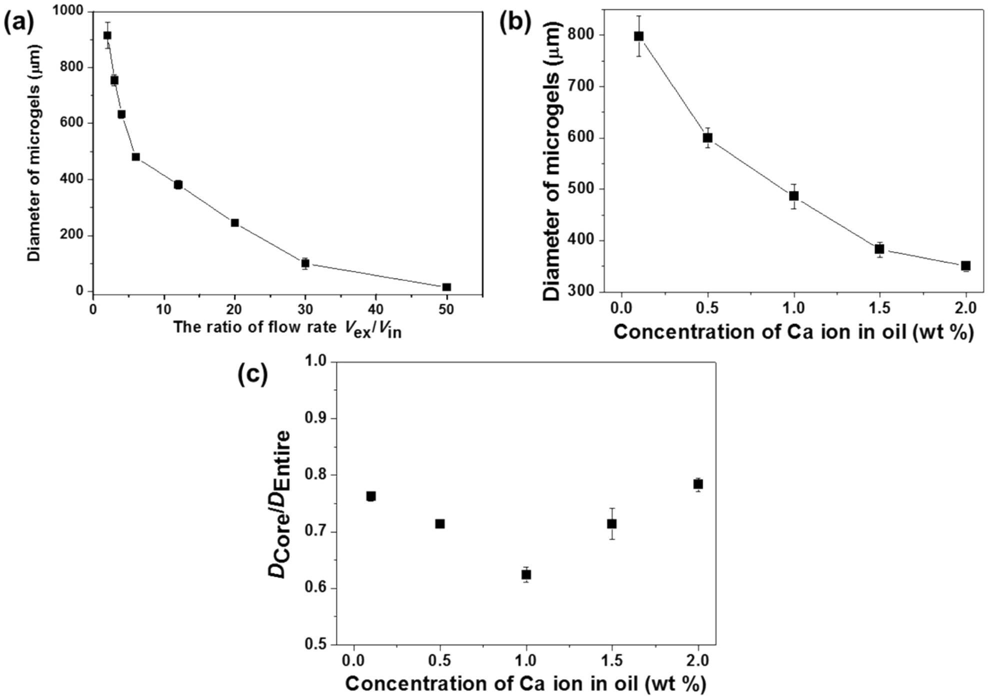

Figure S3. (a, b) Dependence of the overall diameters of hybrid core-shell microgels on the ratio of flow rates (V_{Ex}/V_{In}, where V_{Ex} is the flow rate of continuous oil phase and V_{In} is the flow rate of dispersed aqueous phase) and concentration of Ca^{2+} ions in oil. (c) Dependence of the ratio of the core size to overall size of the hybrid microgels with Au NR cores (D_{Core}/D_{Entire}, where D_{Core} is the core diameter of the hybrid microgels and D_{Entire} is the overall diameter of the hybrid microgels, respectively) on the concentration of Ca^{2+} ions in oil.

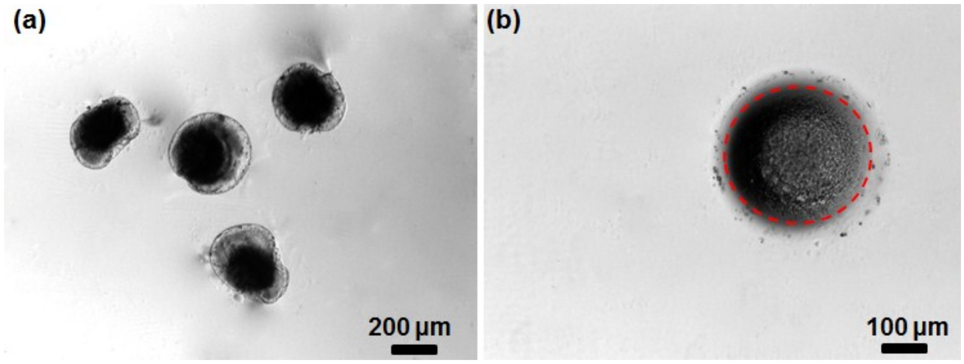

Figure S4. Optical microscopy images of hybrid core-shell microgels made from I-carrageenan (a) and sodium carboxymethylcellulose. Au NRs were used as cores. The red circle indicates the core region of the hybrid core-shell carboxymethylcellulose microgel.

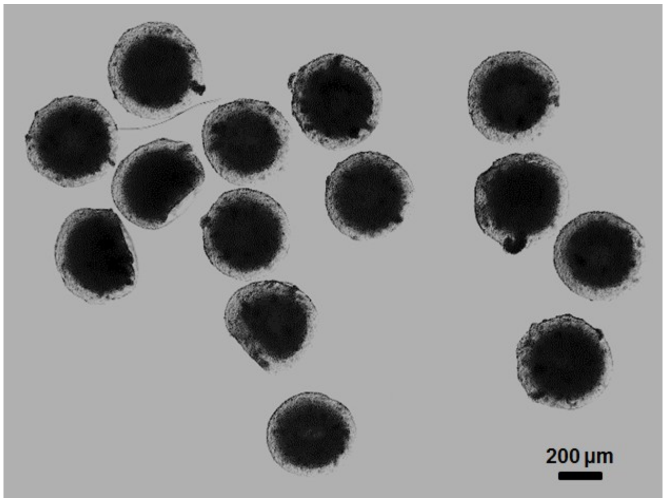

Figure S5. Optical microscopy image of hybrid core-shell microgels with silica NPs and Au NRs in the cores.

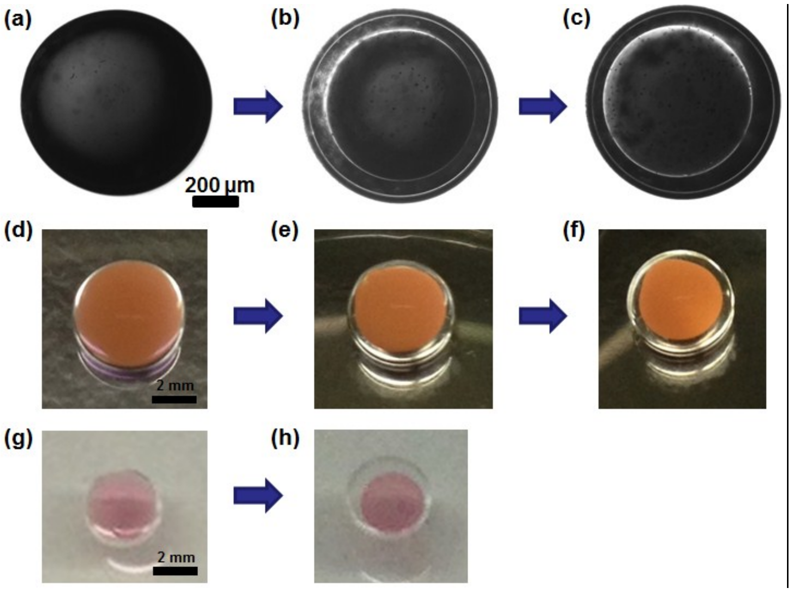

Figure S6. (a-c) Optical microscopy images of the formation process of hybrid core-shell microgels, at different time intervals after the alginate droplets were immersed in a solution of CaI_2 in undecanol: (a) 10, (b) 35, and (c) 60 min. (d-f) Photographs of the formation process of hybrid alginate core-shell microgels with Au NRs as cores (g, h) Photographs of the formation process of hybrid alginate core-shell microgels with Au NPs as cores.

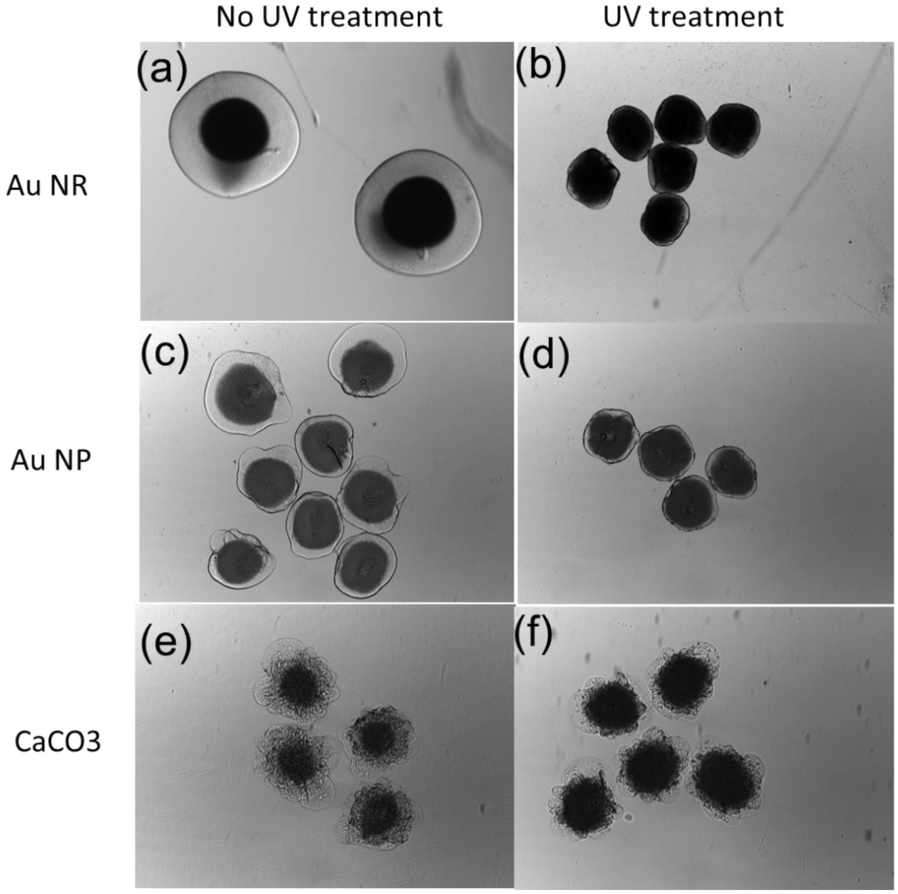

Figure S7. The effect of UV-initiated polymerization on the formation of hybrid core-shell microgels from droplets containing alginate (1 wt%), N-isopropyl acrylamide (8 wt%), N,N'-methylene-bis-acrylamide (5 wt%), and initiator (Irgacure 2959). The droplets containing Au NRs (a, b), Au NPs (c, d) or $CaCO_3$ NPs (e, f) are placed in a solution of CaI_2 (~ 0.1-2 wt %) in undecanol. (a-f) Optical microscopy images of the hybrid microgels obtained from ionic crosslinking of precursor droplets with (b, d, f) and without (a, c, e) UV treatment.

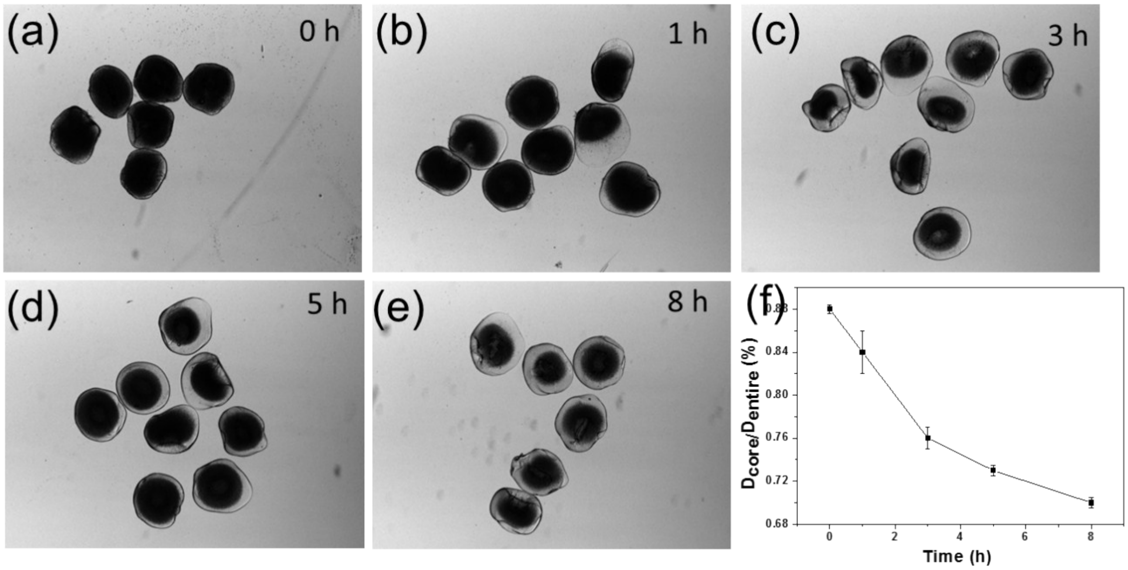

Figure S8. The effect of UV-initiated polymerization on the formation of hybrid core-shell microgels from droplets containing alginate (1 wt%), N-isopropyl acrylamide (8 wt%), N,N'-methylene-bis-acrylamide (5 wt%), and initiator (Irgacure 2959). The droplets are placed in a solution of CaI_2 (~ 0.1-2 wt %) in undecanol and irradiated with UV light after different time periods of ionic crosslinking processs. (a-e) Optical microscopy images of the hybrid core-shell microgels and (f) the dependence of $D_{\mathrm{Core}}/D_{\mathrm{Entire}}$ at different time points of ionic crosslinking.

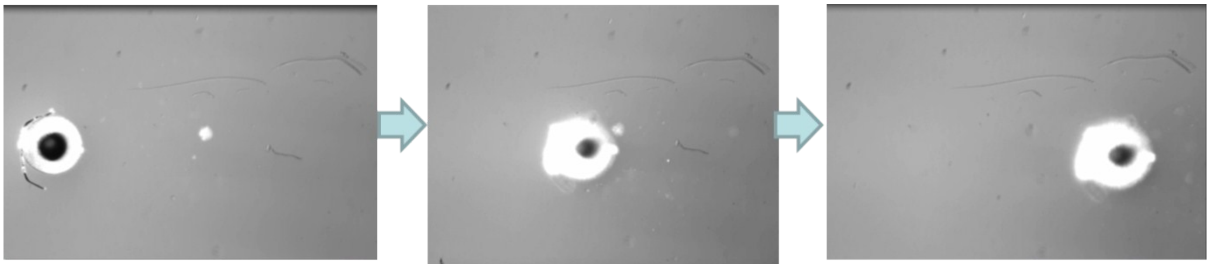

Figure S9. Plasmonic micro-motor based on hybrid core-shell alginate microparticles loaded with Au NRs in the core. The irradiation of the microgels with NIR light from one side of the particle triggered the movement of hybrid core-shell particles, as a result of the asymmetric thermal gradient in the vicinity of hybrid particles due to photothermal effect of Au NRs.

Table S1. Zeta potential measurements of aqueous solutions containing various inorganic NPs, including, Au NPs, Au NRs, silica NPs, CdSe QDs, $CaCO_3$ NPs, and Fe_3O_4, as well as aqueous alginate solutions containing Au NRs or Au NPs.

Item	**Zeta potential**
Au NRs/water	23.8±1.6
Au NPs/water	- 41.9±2.0
Silica NPs/water	- 1.0±0.1
CdSe QDs/water	- 30.0±0.5
$CaCO_3$ NPs/water	15.5±0.2
Fe_3O_4 NPs/water	10.8±0.2
Au NRs/alginate	- 53.2±3.2
Au NPs/alginate	- 57.7±6.3

Table S2. Zeta potential measurements of aqueous alginate solutions containing Au NRs with different concentrations.

Item/(mg/mL)	**Zeta potential**
Au NR/0.2	- 53.2±3.2
Au NR/0.02	- 64.2±5.9
Au NR/0.002	- 60.1±7.7
Au NR/0.0002	- 57.7±5.4
Au NR/0.00002	- 56.2±4.5

Table S3. Zeta potential measurements of aqueous alginate solutions containing Au NPs with different concentrations.

Item/(mg/mL)	**Zeta potential**
Au NP/0.2	- 57.7±6.3
Au NP/0.02	- 59.8±5.1
Au NP/0.002	- 55.8±5.1
Au NP/0.0002	- 55.6±2.7
Au NP/0.00002	- 63.5±7.7