Supporting Information

Deformable, sensible, and reconfigurable microgels with structural colour: Potential as camouflage soft microrobots

Yajing Liu, Xiuyu Wang, Feng Feng, Qilong Li, Hanzhang Xiao, and Li Yao,**

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Chemicals and reagents

The amphiphilic block copolymers (BCPs) of poly(N-isopropylacrylamide)–b–poly(N-vinylimidazole) (PNIPAM-b-NVI), Polyethylene glycol (PEG, Mw ≈ 6000) were purchased from Sigma-Aldrich. The trimethoxy(octadecyl)silane, poly (ethylene glycol) diacrylate (PEG-DA, M_w=700), 2-hydroxy-4-(2-hydroxyethoxy)-2-methylpiophenone, rhodamine B, dimethicone, span80, trifluoroacetic acid, poly(vinylalcohol) (PVA), M-280 microgels, propyl amine were purchased from Aladdin. The magnetic Fe_3O_4 nanoparticles with PEG modified were synthesized via ligand exchange.

Preparation of PEG modified Fe_3O_4 nanoparticles

The first step is to synthesis oil dispersed Fe_3O_4 nanoparticles of about 4 nm in diameter following the procedure previously reported in the literature[1,2]. Generally, a mixture of $Fe(acac)_3$ (2 mmol), phenyl ether 10 mL, oleic acid (6mmol), oleylamine (6 mmol) and 1,2-hexadecanediol (15 mmol) was magnetic ally stirred under the protection of N_2. The mixture was heated to heated to 180 °C for 30 min and then refluxed at 265 °C for other 30min under a flow of nitrogen. After cooled to room temperature, 30 mL ethanol were added, the black materials were precipitated. The black product was washed with ethanol for three times, and finally dissolved in hexane. The second step is to synthesis PEG modified Fe_3O_4 nanoparticles

via ligand exchange. As a typical example, PEG diacid (100 mg) were dissolved in a mixture solvent containing 3 mL tetrahydrofuran (THF) and 2 mL hexane Fe_3O_4 solution (5 mg). The solution was stirred at 45 °C for 12 h. Finally, the black sediments were obtained after treating with hexane, and dried under vacuum at room temperature. The final powders were readily dissolved in water, supporting that the PEG coating was effectively realized.

Assembly of the microfluidic devices

To generate monodisperse emulsion droplets of well-controlled sizes, we construct microfluidic devices by assembling glass capillaries on a glass slide. The inner capillary was tapered to the required size 30-120 μm by microelectrode puller P-97 (Sutter Instrument Co, U.S.A.). After cleaning with ethanol, the inner capillary was modified with ocadecyl trimethoxylsilane and then dried by nitrogen. Then the tapered end of the inner capillary was coaxially nested into the outer square capillary with an inner diameter of 1.05 mm (VitroCom, Inc.), and sequentially assembled on a glass slide. The dispersed phases flowed through the inner capillary; and the continuous phase flowed via the interstices between the inner and the outer capillaries.

Fabrication of topographically heterogeneous microgels.

Typically, the continuous phase contained the low viscosity silicone oil (KF-96, 50cst) and Span80 surfactant (2 wt%), flowing pass through the interstices between the inner and the outer capillaries. The disperse phase of PNIPAm-*b*-Vim (1wt%) aqueous solution flowed through the inner capillary. The two phases were pumped into the capillary microfluidic devices by using syringe pumps (PHD 2000 series, Harvard Apparatus) with controlled flow rates. The droplet diameters can be readily tuned from 30 to 500 μm by the size of the orifice and the flow rates of the two phases. The formation process of droplets was monitored by using an optical microscope (IX71, Olympus) equipped with a high-speed camera. The

monodisperse fresh droplets were collected in a hydrophobic dish. For fabrication of temperature stimulus, the collected emulsions were placed in the 40 ^{o}C external environment for 50 min. In order to achieve the pH stimulus, the fresh droplets were directly collected placed in acidic buffer solvent for 1h. The pH was adjusted to above and below pH=6.4 by addition of trifluoroacetic acid and propyl amine. PEG-Fe_3O_4 (1wt%) magnetic nanoparticles and PNIPAm-b-VIm (1wt%) aqueous solution were uniformly mixed and were added into the dispersion phase. The generated droplets were collected in container and then the container was put above a Nd-Fe-B sintered magnet at a special angle for about another 50 min at room temperature.

Photopolymerization of continuous topographically heterogeneous microgels.

The UV light source was provided by a 100 W mercury lamp and an 11000v3 UV filter set by Chroma Technology Corp. For droplets photopolymerization, UV light was focused onto a specific location through microscope.

Characterization

Sequential optical images for emulsion evolution were monitored using Olympus IX71 optical microscope. The resulting products morphologies were observed by SEM and ESEM. SEM images were taken on a S4800 scanning electron microscopy at an accelerating voltage of 150 kV. ESEM images were taken on a Quanta-200 scanning electron microscopy at an accelerating voltage of 30 kV. And the elemental compositions of samples were also analyzed using a S4800 scanning electron microscopy equipped with an EDS unit. Before imaging, the SEM samples were coated with a thin layer of gold (14 nm). Transmission electron microscopic (TEM) images of the magnetic nanoparticles were using a JEM-2011 microscope at an accelerating voltage of 200 kV. Atomic force microscopy (AFM) measurements of the Young's modulus of THGM and microgels M-280 were performed using a commercial AFM Nanoscope IIIa (Bruker, USA)

in Force Volume (FV) mechanical imaging mode with medium resolution during imaging (64 x 64), which allows for much clearer, quantitative evidence. Using IX83 inverted fluorescence microscope, the excitation wavelength was 488 nm, and the color pictures of anisotropic microgels were obtained.

Additional Characterization Data

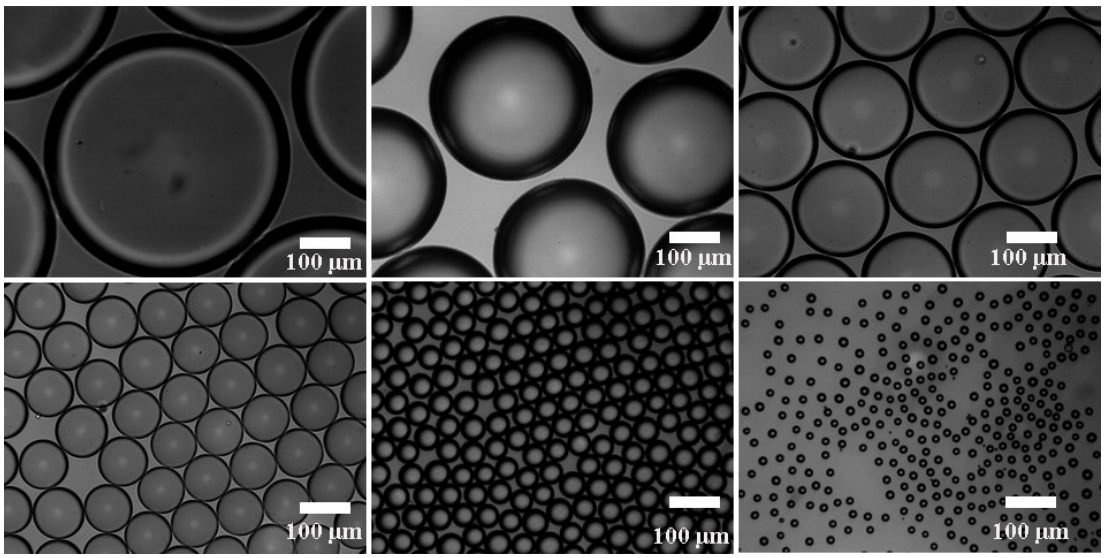

Fig.S1. Optical microscopy images showing the different size of microgels by adjusting the outer flow rate and inner flow rate. The scale bar is 100 μm.

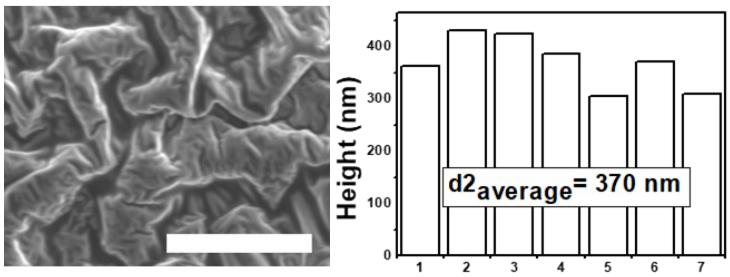

Fig. S2. SEM images showing labyrinth pattern and the thickness. The scale bar is 500 nm.

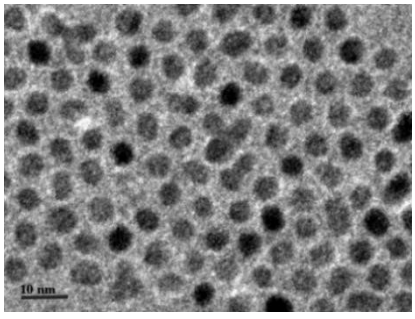

Fig. S3. TEM image of individual PEG-coated Fe_3O_4 nanoparticles.

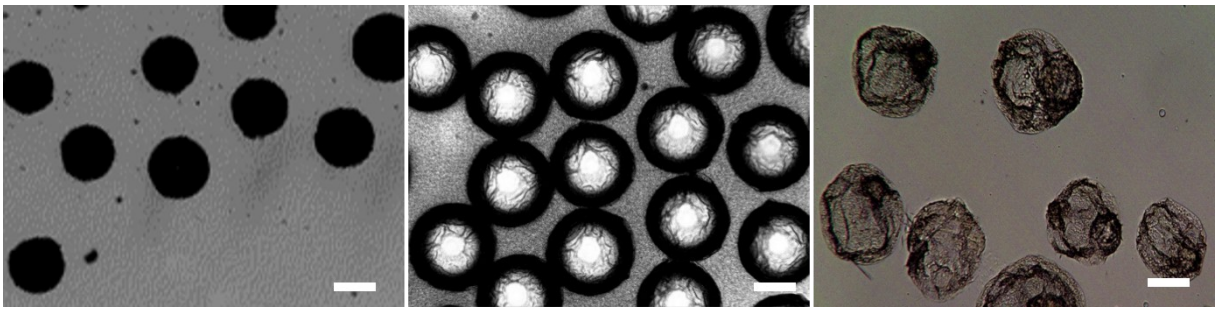

Fig.S4. Physical appearance of topographically heterogeneous micromaterials of Optical microscopy images in different assembly conditions. (a) Solidified structure of pure MNPs droplets without BCP, (b) pickering structure show pure BCP without MNPs, (c) Janus structure show 30 wt% MNPs and BCPs. The scale bar is 100 µm.

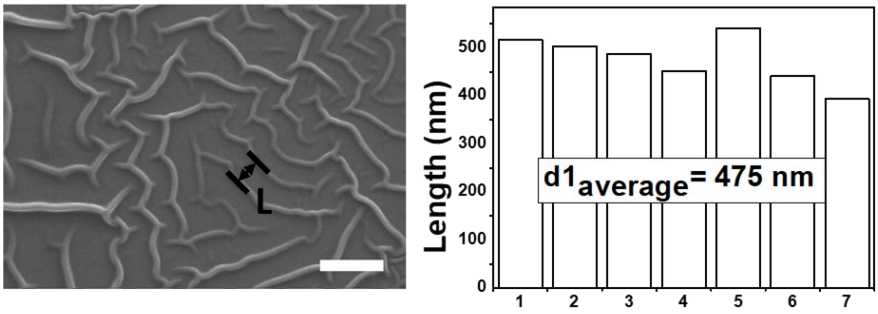

Fig. S5. The SEM images show the labyrinth and generating a 1D array of periodic wrinkles with a periodicity of L ≈ 500 µm. The scale bar is 1 µm.

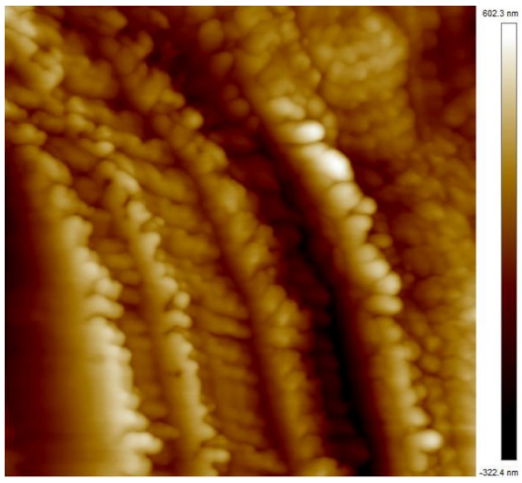

Fig. S6. AFM image of the structure of THGMs.

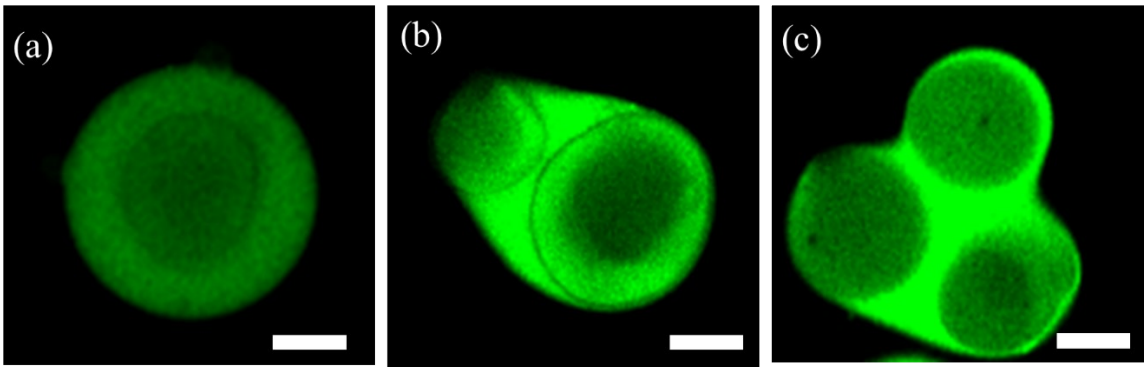

Fig. S7. Confocal laser scanning microscopy images and corresponding bright field images of (a) yolk-shell structure, (b) snowman-like geometry structure, (c) triangle structure. The scale bar is 100 μm.

References

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[2]S. H. Sun, H. Zeng, D. B. Robinson, S. Raoux, P. M.Rice, S. X. Wang, G. X. Li, J. Am. Chem. Soc. 2004, 126, 273.