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A side-by-side capillaries-based microfluidic system for synthesizing size- and morphology-controlled magnetic anisotropy janus beads

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ABSTRACT

With two segments having different chemical or physical properties, janus particles have gained widespread attention in recent years. A fast assembly–disassembly side-by-side capillaries-based microfluidic system was designed for rapid and easy generation of janus particles with magnetic anisotropic properties. Two immiscible organic phases, among which one contained magnetic particles, were emulsified by a stream of an aqueous phase into janus droplets formed at capillaries' tips and transported after breakup by the continuous aqueous phase in an outlet tubing. Then upon downstream UV irradiation, droplets were hardened into solid janus microparticles containing magnetic particles in one of their two segments. By changing the flow rates of organic and aqueous phases, not only the overall size of janus particles but also the relative volume of the two hemispherical segments could be controlled. Generated janus particles were proved having magnetic anisotropy by their forced-driven rotation in an external magnetic field, which makes them potentially interesting materials in chemical and biomedical applications.

1. Introduction

Since discussed by de Gennes in his Nobel Prize lecture in 1991 [1], janus particles have gained increasing attention in recent years. They are named after the Roman god with two faces looking into opposite directions who represents dichotomy [2]. Thus, janus particles are composed of two segments of different chemical and/or physical properties. What intrigued de Gennes most was the unique advantage of amphiphilic particles at interfaces [2,3]. The monolayer formed by such kind of particles behaves like a "breathing skin", allowing small molecules to diffuse through the gaps between the janus particles. Due to their unique morphology, janus particles differ from more conventional isotropic particles. Janus particles with diverse functions have great potential in applications such as emulsion stabilization [4,5], optical probes for biological interactions and rheological measurements [6], sensors [2,7,8], self-assembly of building block components [9] and medical field [10]. In particular, particles with magnetic anisotropy have recently attracted a lot of interest in biomedical applications, for example, drug delivery [11], detection in magnetic resonance imaging [8], nucleic acids separation [12] and so on, owing to their controllable rapid-response to an external magnetic field.

To promote the practical use of janus particles, various methods could be considered. Physical approaches such as a selective masking tools combined with gold evaporation [10,13], colloidal crystallization [9,10,13], microcontact printing [9,10,13] and electrical jetting [8–10,13,14] have been developed. However, all these methods suffer from difficulties to achieve a large volume production and thus are limited in their widespread use [9,13]. Recently, Ning et al. [14] have presented a facile route to the production of janus microspheres with dual anisotropy of porosity and magnetism based on Pickering-type double emulsions. Although this method is simple and easy to scale up, it suffers from the limited control on size and morphology. Other chemical methods such as manipulation of growth and nucleation of molecular species during precipitation, or the template-assisted manipulation of spherical particles face the same difficulties [15].

On the other hand, microfluidic technologies have been found to be very helpful for the production of monodisperse droplets and were further employed for the preparation of functional microparticles. When composed of a polymerizable liquid, the dispersed droplets can be easily hardened downstream into solid particles either by UV- or thermally-induced polymerization [16]. Compared to conventional processes, microfluidic methods enable

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a precise control over particle size, shape, morphology and composition [16–18]. Furthermore, a scale-up approach by multiplexing several individual microfluidic systems can lead to large increase in throughput as reported by Nisisako et al. [13].

Two distinct categories of microfluidic devices have been identified for the production of micron-range droplets: microchannel-based and capillary-based microsystems. Several studies have successfully demonstrated microfluidic synthesis of magnetic anisotropic particles based on microchannel-based system. Weitz and co-workers [15] synthesized magnetic hydrogel particles with anisotropic features using double emulsions as templates in a microchannel device. To our knowledge, very few studies have been reported focusing on the preparation of janus particles using capillary-based microsystems. The main advantages of capillary-based microfluidic devices are (i) off-the-shelf components, (ii) assembly within few minutes, no lengthy microfabrication process are required (e.g. photolithography, milling, anodic bonding, etc.), (iii) relative easiness to keep the dispersed phase away from the wall of the device which prevents any phase inversion and leads to microfluidic device that can be used for the production of O/W or W/O emulsions [19].

In this paper, a facile route was presented for the generation of janus particles with anisotropy of magnetism by means of a side-by-side capillaries-based microfluidic device. The overall size of janus particles (size range 250–800 μm) and the fraction of two hemispherical parts can be readily controlled by adjusting the dispersed and continuous phase's flow rates. In addition, the controlled rotation of janus particles was demonstrated in an external magnetic field.

2. Experimental

2.1. Materials

An aqueous solution of sodium carboxymethyl cellulose (CMC, Sinopharm Chemical Reagent Co., Ltd.) was used as the continuous phase. For the dispersed phases, one contained tri(propylene glycol) diacrylate (TPGDA, Tokyo Chemical Industry Co., Ltd.) and 1-hydroxycyclohexyl phenyl ketone (HCPK) as a photoinitiator (Bide Pharmatech Ltd.); the other one was consisted of kerosene (Shanghai Hasitai Oil Co., Ltd.), 4–6%(methacryloxypropyl) methyl siloxane–dimethylsiloxane copolymer (Beijing HWRK Chemical Technology Co., Ltd.), 1-hydroxycyclohexyl phenyl ketone (HCPK) as a photoinitiator (Bide Pharmatech Ltd.) and magnetic particles. TPGDA and 4–6%(methacryloxypropyl) methyl siloxane–dimethylsiloxane copolymer were chosen as dispersed phases because they are immiscible which is the basis of the formation of janus-morphological droplets and they are both UV curable. Ferric chloride hexahydrate ($FeCl_3{\cdot}6H_2O$), ferrous sulfate heptahydrate ($FeSO_4{\cdot}7H_2O$), sodium hydroxide (NaOH), ethanol and ethyl acetate were purchased from Sinopharm Chemical Reagent Co., Ltd. for the preparation of magnetic particles.

2.2. Preparation of magnetic particles

Magnetic particles were produced by co-precipitation of Fe^{3+} and Fe^{2+} (2:1 M ratio) with NaOH. In brief, the required amount of $FeSO_4{\cdot}7H_2O$ and $FeCl_3{\cdot}6H_2O$ were dissolved in distilled water. The mixed aqueous solution was heated at 60 °C for 1 h while being stirred. The pH of the mixture was increased to 11–12 by the addition of NaOH solution using atomizer (Shanghai Jiahua United Co., Ltd.). After vigorously stirred and cooling to room temperature, the precipitated particles were washed several times with ethanol and ethyl acetate. The mean size of the synthesized magnetic particles was 50 nm.

2.3. Side-by-side capillaries-based microfluidic device

The microfluidic device (Fig. 1) was designed to accommodate two hydrophilic capillaries with inner/outer diameter of 252 μm/358 μm (Fused silica tubing, Polymicro Technologies), a PTFE outlet tubing with inner/outer diameter of 1600 μm/3200 μm (Polytetrafluroethylene, Fisher Scientific Bioblock), a T-junction and two line junctions (Upchurch Scientific).

The two capillaries were inserted in a side-by-side arrangement along the main axis of the T-junction and both tips placed at same location in the centerline of the outlet tubing. Dispersed and continuous phases were delivered by means of three syringe pumps (LSP01-1A, Longer Pump) through the capillaries and T-junction's inlet respectively. Upon contact with the continuous phase at capillaries' tips, the two immiscible dispersed phases formed a single meniscus with two different segments composed of each dispersed phase (Fig. 2) which ultimately broke up to release a janus droplet under the shear imposed by the flow of the continuous phase. Then the droplet was conveyed by the flow of the continuous phase in the PTFE tubing.

2.4. Polymerization and characterization

Further downstream, generated janus droplets were hardened on the fly by photopolymerization thanks to an UV light source operating at 18 W/cm^2 which is set 10 cm away from the PTFE Tubing (Shandong Zibo Lighting Co., Ltd.). Before exposed to the UV lamp, it took about 2.5 min for the continuous flow to convey the prepared janus droplets. After 3 min UV irradiation, the janus droplets were firmly consolidated. The meniscus breakup into janus droplets was monitored by an optical microscope (XSP-30E, Shanghai Halibut Instrument Limited Company) equipped with a CCD camera (uEye UI-2220SE, IDS). The overall janus particle size and sizes of its two parts were observed and analyzed using the image analysis module of the CCD camera software (uEye Cockpit). The camera captured up to 52 fps at a full resolution of 768 $\times$ 576 pixels.

2.5. Magnetic orientation

Fig. 2 shows the schematic experimental setup for forced-driven orientation. Janus particles were deposited in a glass garden and suspended in an aqueous solution of CMC to (i) prevent any sticking to the glass surface and (ii) allow free rotation. A magnet with size of 100 mm * 50 mm * 10 mm and remanence of 1.44–1.48 T was put 5 cm away on one side of the glass garden and then was rotated to generate a rotating magnetic field. The rotational speed of the magnet is 6.5°/s. Induced-rotation of janus particles was observed under optical microscope and recorded by the CCD camera.

3. Results and discussions

3.1. Generation of janus particles

Before janus droplet generation, the two polymerizable dispersed phase solutions and continuous phase solution were prepared first according to the weight composition reported in Table 1. After washing with ethanol and ethyl acetate to remove water, the prepared magnetic particles were mixed with dispersed phase II. Other researchers have found that alkyl silane could improve pigment dispersion [20] which corresponds to our experimental result that magnetic particles have a better dispersity in dispersed phase II compared with dispersed phase I. With the help of a planetary ball mill (Changsha Tianchuang Power Technology Co., Ltd.), the