Magnetically responsive elastic microspheres

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We report the design, fabrication, and characterization of magnetically responsive elastic microspheres consisting of polydimethylsioxane (PDMS) and magnetic nano-/microparticles. The microspheres can have either core-shell or solid structure, fabricated by using a microfluidic technique. The mechanical characteristics are determined with a modified electronic balance, and the results show that the microspheres exhibit magnetostrictive effect. Such microspheres can in addition behave as a smart material controllable through an external magnetic field. Owing to the transparency, biocompatibility and nontoxicity of PDMS, the magnetically responsive elastic microspheres may have potential applications in drug delivery, biosensing, bioseparation, and medical diagnosis. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2830620]

Magnetorheological (MR) fluid is a type of colloids whose viscosity varies with applied magnetic field strength.[1,2] The field-induced tunable mechanical properties of MR fluid have already found applications in MR clutch, automobile suspension system, surface polishing etc.[3,4] Elastomers such as rubber are traditional materials which have wide applications in damping mechanical vibrations and impact dissipation.[5,6] Recently, a type of elastomers, composed of ferromagnetic (or ferrimagnetic) particles dispersed in solidified rubberlike material, which exhibits dramatic changes in mechanical properties such as elastic modulus or hardness when subjected to a magnetic field has been fabricated.[7,8] One obvious advantage of such elastomers is that there is no sedimentation issue, in contrast to a MR fluid. These magnetic particle-embedded elastomers have wide potential applications in adaptive vibration absorbers, stiffness tunable mounts, automobile suspensions, and variable impedance surfaces.[8–10]

In this letter, we present a capillary microfluidic technique to fabricate two types of magnetically responsive elastic microspheres with appreciable magnetostriction effect. The microspheres are based on polydimethylsioxane (PDMS) and magnetic nano/microparticles. The first type of microspheres has the core-shell structure in which the MR fluid or magnetic colloid is encapsulated in a PDMS shell. The second type is in the form of solid microspheres synthesized from a mixture of magnetic nano-/microsized particles embedded in a PDMS matrix. The use of PDMS is important in the functionality of the microspheres, not only because of its good elasticity, but also due to its thermally maneuverable solidification process. The PDMS-based magnetrostrictive microspheres are transparent, biocompatible, and nontoxic. These are the desirable characteristics for potential applications in drug delivery, biosensing, bioseparation, and medical diagnosis.[11–13]

A microfluidic flow-focusing device (MFFD) was constructed to generate our microspherical elastomers.[14–16] Figure 1(a) shows the schematic design of the MFFD, consisting of a main channel (900 μm in width and in depth) in bulk PDMS. The microfluidic chip was fabricated by first fixing the desired plexiglass channel mold, generated by laser cutting on a plexiglass substrate (laser cutting machine MT-MC-SERIES). PDMS gel was poured on the mold and placed in vacuum for 20 min to ensure layer uniformity. After curing, the PDMS layer with embedded channels was easily peeled off. Two glass capillaries (~150 μm in inner diameter) were inserted at the two intersections, serving as an entry way for

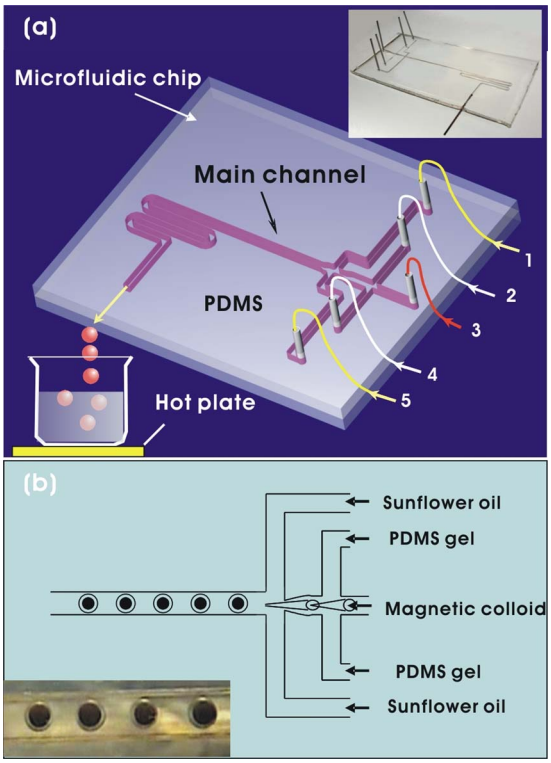

FIG. 1. (Color online) (a) Schematic picture showing the MFFD design and construction. The overall chip size is $8\times4\times0.4$ cm. The right upper inset is a photograph of the chip. (b) Schematic illustration of the microsphere production process in MFFD, where the different injected phases are in correspondence with inlets 1–5 in Fig. 1(a). The left lower inset is an optical microscopic image of the core-shell microspheres formed in the MFFD channel.

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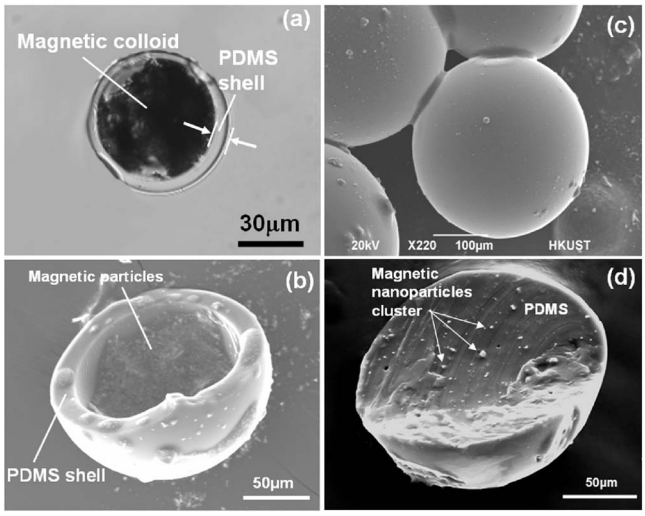

FIG. 2. (a) An optical image of a core-shell structured microsphere. Magnetic colloid consisting of Fe_3O_4 nanoparticles and sunflower oil is encapsulated by a PDMS shell. (b) The cross-sectional SEM image of a core-shell microsphere. Here, some magnetic particles are seen to adhere to the inner wall of the cavity. (c) The SEM image of solid microspheres. (d) The cross-sectional SEM image of a solid microsphere, wherein the Fe_3O_4 nanoparticle clusters are randomly dispersed in the PDMS matrix.

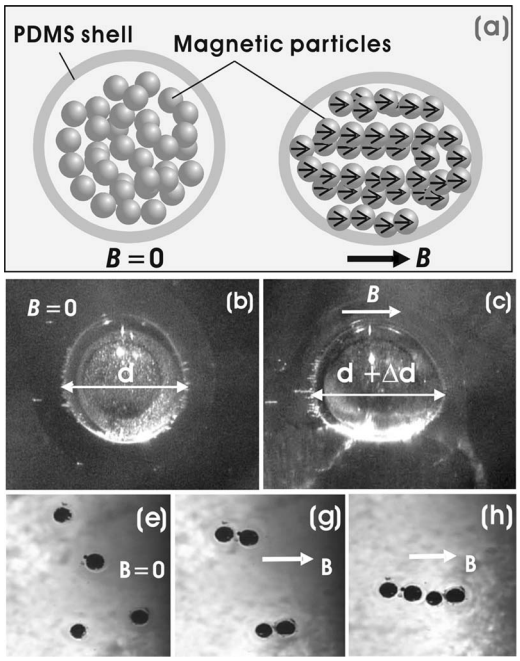

FIG. 3. (a) A cartoon depicting the response of magnetic particles encapsulated in a core-shell microsphere subjected to an external magnetic field. (b) A single core-shell microsphere suspended in sunflower oil. (c) When exposed to a magnetic field of 3000 G, the deformation of core-shell microspheres is clearly observable. [(c)–(f)] Time sequence evolution of a dipolar chain formation when several core-shell magnetic microspheres were placed under a magnetic field of 3000 G.

the discontinuous phase and a flow-focusing orifice, respectively [see Fig. 1(b)]. The gaps between the glass capillaries and the inner channel wall were seen to be filled with PDMS gel to prevent stream branching. The five inlets for injected streams and an outlet for microsphere generation were configured so that three separate phases could be introduced into the channel. The prepared PDMS layer was subsequently bonded to another half-cured PDMS layer to form sealed channels. The chip fabrication was completed after annealing at 60 °C for 30 min. A photograph image of the chip is shown in the right upper inset of Fig. 1(a).

The microsphere fabrication procedure is summarized as follows. For the outer two streams (channels 1 and 5), the sunflower oil (Soon Hup Co. Ltd.) with viscosity η_{sun} =60 mPa was chosen as the carrying fluid, owing to its nonwetting characteristic with the PDMS channel. The diluted PDMS gel [by silicone oils at a concentration of 77% (w_{PDMS}/w_{sum})] with a viscosity of 600 mPa was supplied to channels 2 and 4. Magnetic colloid (viscosity η_{mag} =140 mPa), consisting of magnetic nanoparticles (Fe_3O_4) dispersed in sunflower oil at a particle concentration of 30% (w_{Fe3O4}/w_{sum}), was injected at the central channel 3 to serve as the discontinuous phase, shown in Fig. 1(b). The pressure gradient along the main channel resulted in the forward movements of the magnetic colloid, the PDMS gel coming from the orifice surrounding the center capillary, as well as the stream of sunflower oil. With the proper adjustment of flow ratios for the five streams, the PDMS gel and magnetic colloid formed a coaxial jet with a magnetic colloidal core enveloped by a PDMS shell. The coaxial jet extended into the downstream channel before broke up into segments. Due to the action of interfacial tension, the segments rapidly acquired a spherical shape [inset of Fig. 1(b)]. The break-up process was very stable, and uniform microspheres were obtained. The nonwetting character of sunflower oil with PDMS has been useful in preventing the PDMS gel from touching the main channel wall. The solidification of the core-shell microspheres was carried out in a beaker containing sunflower oil heated to 120 °C [Fig. 1(a)]. Under this relatively high temperature, the PDMS gel was rapidly cured. The solid and monodispersed microspheres were obtained by continuously stirring the oil during the solidification process. In our experiment, the same microfluidic device was also used to fabricate the solid microspheres consisting of magnetic particles embedded in PDMS matrix. This was done by replacing the PDMS gels in channels 2 and 4 with PDMS-based mixtures (viscosity η_{col}=830 mPa) consisting of PDMS gel, silicone oil, and magnetic particles (at a particle concentration of 20 w %). For this application, the central channel was out of use.

Figure 2(a) shows a typical optical image of core-shell structured microspheres, wherein the transparent PDMS shell and core filled with magnetic colloid (Fe_3O_4 nanoparticles suspended in sunflower oil) are clearly visible. The corresponding scanning electron microscope (SEM) cross-sectional image of the core-shell microsphere can be seen in Fig. 2(b), where the central cavity can be filled with magnetic colloid. The SEM image for the solid microspheres is shown in Fig. 2(c). In contrast to the core-shell structure, the magnetic nanoparticle clusters are randomly dispersed in PDMS, as can be seen from the cross sectional SEM image shown in Fig. 2(d).

The magnetic response of the core-shell elastic microspheres is shown in Fig. 3. From Fig. 3(a), our experiments show that in the absence of a magnetic field, the magnetic particles were randomly suspended in the PDMS capsule. When an external magnetic field was applied, the magnetic particles formed chains aligned along the field direction, owing to the dipole-dipole interaction between the particles. When the field strength was increased, the core-shell microspheres were stretched along the field direction as seen from Figs. 3(b) and 3(c) for a single core-shell microsphere. The maximum observed deformation $\Delta d/d$ of a core-shell micro-

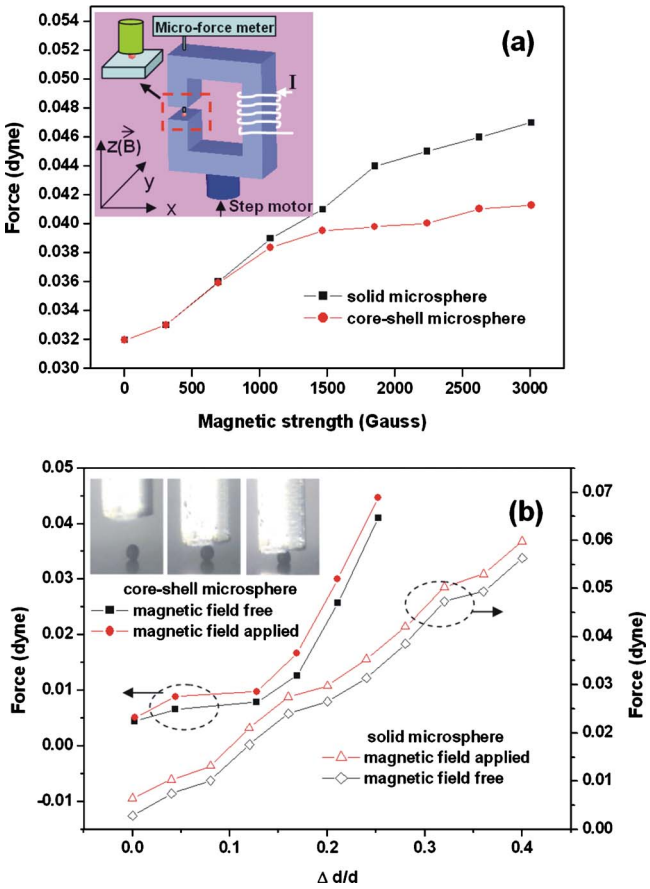

FIG. 4. (Color online) (a) Measured force acting on the microsphere vs applied magnetic field. The schematic experimental setup is shown in the left upper inset. (b) The forces vs relative deformation $\Delta d/d$ (caused by the step motor stage) were measured with and without the application of a magnetic field of 3000 G, where for the cases of a core-shell microsphere (solid symbols) and a solid microsphere (hollow symbols) are indicated with dotted left and right circles, respectively. The left upper inset in (b) depicts the force-measuring rod and the microsphere in noncontact, just touching, and deformation contact positions, respectively.

sphere was 6.3% when the magnetic field strength reached 3000 G. We have also observed the time evolution of several randomly dispersed core-shell microspheres, capsulated with Ni particles, when a magnetic field was applied. The results are shown in Figs. 3(d)–3(f). It is seen that the microspheres formed a chain, aligned along the field direction.

To have a more quantitative understanding of the mechanical properties of both the core-shell microspheres and solid microspheres, we studied their magnetostrictive effect by using a setup schematically illustrated in the inset of Fig. 4(a). Two identical "U"-shaped arms were bonded together to form a horseshoe electromagnet with a 5 mm gap. The electromagnet was driven by a direct current amplifier [see inset to Fig. 4(a)]. The deformation process of the spherical elastomer was *in situ* monitored by a charge coupled device camera and recorded with a video recorder. A plastic rod (1 mm in diameter), with one end linked to a microforce meter and the other passing through a hole drilled on an opened arm, just touched the surface of the microsphere. In the experiment, the plastic rod was first adjusted to ensure that it did not touch the wall of the drilled hole. The microforce meter was modified by a precision weighting balance (OHAUS, ANALYTICAL Plus) with an accuracy of 0.01 mg. The stage holding the setup was driven up and down by a step motor with a step size of 5 μm.

The force acting on the microsphere, measured as a function of applied magnetic field, is shown in Fig. 4(a). In the experiment, the force was reset to zero when the rod end just contacted the microsphere in the absence of a magnetic field. The application of a magnetic field led to an elongation of the microsphere along the field direction. The resulting push against the rod could cause a measurable deformation force. As seen from Fig. 4(a), the measured deformation force for the two types of microspheres (core-shell and hard microspheres are shown as left and right dotted circles, respectively) increases monotonically as a function of applied magnetic field, and tends to saturation when the field strength is above 1500 G. In Fig. 4(b), the measured deformation force is plotted as a function of $\Delta d/d$. For fixed $\Delta d/d$, there can be two values—one under the application of a magnetic field and the other without the application of a magnetic field. Here the deformation was caused by the step motor driving the stage upward in measured amount, and the force was measured by a microforce meter. It is seen that at 3000 G of applied field, there is a clear increase in the measured force by ~5 mdyn at a fixed value of $\Delta d/d$. In other words, Fig. 4(b) shows an increase in the deformation modulus. Since PDMS is magnetically inactive, this increase must be due to the interaction of ferromagnetic particles with the applied magnetic field, plus the interaction between magnetized particles.[17] These experimental results suggest that, for both the core-shell and solid microspheres, (1) the stretch increases with the applied magnetic field and (2) the composite hardens under an applied field. The differences between the two types of microspheres are (1) the stretch of the core-shell microsphere tends to saturate earlier when the magnetic field reaches some critical value [Fig. 4(a)], and (2) the core-shell microsphere is less compressible [Fig. 4(b)].

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