Electronic Supplementary Material (ESI) for Nanoscale Horizons.

Electronic Supplementary Information

Magnetically Tunable Colloidal Micromirrors

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Experimental

Reagents

Methanol, denatured ethanol, isopropanol, cyclohexane, and acetone were purchased from Fisher. Poly(diallyldimethylammonium) chloride (PDDA, MW = 400,000-500,000, 20 wt % in H_2O), oleic acid, iron pentacarbonyl, and tetramethylammonium hydroxide (TMAH, 25 wt % in H_2O) were purchased from Sigma-Aldrich. $HAuCl_4 \bullet 3H_2O$, octadecene (ODE), tetraethylorthosilicate (TEOS), NH_3 (~ 29 wt % in H_2O), and (3-aminopropyl) triethoxysilane (APTES) were purchased from Acros. Salicylic acid was purchased from MP Biomedicals, and agarose was purchased from Biorad. All reagents were used as received without additional purification.

Au plate synthesis

Au microplates were synthesized using an acid-mediated reduction method modified from a previous publication.[1] In a typical synthesis, DI water (70.2 mL), PDDA (1.8 mL, diluted to 2 wt % in H_2O), and salicylic acid (8 mL, 18.1 mM) were heated to 80 °C in an Erlenmeyer flask under stirring. The reaction was then initiated by adding $HAuCl_4$ (3.2 mL, 48.6 mM), after which the solution was stirred for 10 min to yield a turbid, golden solution. The solution was then cooled and centrifuged in six 15 mL centrifuge tubes at 4000 rpm for 4 min, after which the supernatant was decanted with a pipette. The remaining

contents of the six tubes were then combined into a single 50 mL centrifuge tube, and were washed in water 8 times for 5 minutes at 11000 rpm. Finally, the Au microplates were dispersed in 2 mL of DI H_2O to produce a suspension with a final concentration of 55 mg/1 mL. The resulting microplates had an average diameter of 7.28 ± 2.61 μm and a thickness of ~ 75 nm.

Synthesis of superparamagnetic nanoparticles

γ-Fe_2O_3 nanoparticles were synthesized using a high-temperature oil-phase protocol.[2] This method is utilized because it produces high yields of monodisperse nanoparticles with magnetic susceptibility values near that of the bulk material. First, 100 mL of ODE was mixed with 9 mL of oleic acid and degassed with N_2 for 1 hr at 100 °C. Next, 2 mL of iron pentacarbonyl was injected into the solution, which was then heated to 295 °C, leading to a color change in the solution from orange to black. After the solution became black and completely opaque, the solution was further heated for 1 hr at the same temperature. Afterwards, the solution was cooled to 200 °C and air was gently bubbled in for 2 hrs. Finally, the solution was cooled to room temperature, yielding a ferrofluid consisting of 16.5 ± 1.2 nm γ-Fe_2O_3 nanocrystals. The particles were then processed by dividing the solution into ten 50 mL centrifuge tubes and adding 20 mL of acetone to each. The samples were then centrifuged for 6 min at 10000 rpm, after which the supernatant was removed and the samples were combined into two tubes, to which 10 mL of cyclohexane was added (to each) to disperse the pellets, followed by 20 mL of acetone. The samples were then centrifuged for 5 min at 9000 rpm, and were washed one more time. Finally, the samples were combined and dispersed in 10 mL of cyclohexane.

Phase transfer of magnetic nanoparticles

The ferrofluid was subsequently transferred to the aqueous phase using a published method.[3] Briefly, 1 mL (10 %) of the ferrofluid in cyclohexane was added to 3 mL of acetone and placed in two 2 mL centrifuge tubes. The sample was sonicated for 1 min, then centrifuged for 5 min at 15000 rpm, after

which the acetone was removed and the sample was allowed to sit uncapped for 10 min to evaporate residual acetone. The samples were then dispersed in 10 mL of TMAH (diluted to 10 wt % in H_2O), sonicated for 15 min, and aged for 1 hr, after which the sample was separated out with a magnet and the solution was decanted. 5 mL of TMAH was then added to the sample, which was sonicated for 15 min and aged for 1 hr; the sample was again separated out with a magnet and the TMAH was poured off. This process was repeated one more time, after which the sample was finally dispersed in 5 mL of DI H_2O.

Amine functionalization of maghemite nanoparticles

The maghemite particles were coated with SiO_2 using a modified Stöber process. Typically, 1 mL (20%) of the ferrofluid sample dispersed in H_2O was added to 20 mL of denatured ethanol, to which 2 mL of DI H_2O and 50 µL of TEOS was also added. The reaction was then initiated by adding NH_3 (1 mL, 29 wt % in H_2O), and the solution was covered and stirred for 20 minutes. Afterwards, the solution was centrifuged 4 times and washed with ethanol 3 times via centrifugation at 15000 rpm for 10 min. The sample was dispersed in 5 mL of isopropanol, then washed in methanol 4 times, isopropanol 2 times, and finally dispersed in 5 mL of isopropanol. Likewise, amine functionalization of the nanoparticles followed a previous recipe.[4] The sample was then added to 15 mL of isopropanol in a 3-neck flask connected to a water-cooled jacketed condenser, to which 5 µL of APTES was added. The solution was then heated to reflux at 80 °C for 2 hrs, cooled, and washed 3 times in ethanol, until finally the sample was suspended in 5 mL of DI H_2O to produce an aqueous, amine-functionalized maghemite nanoparticles with a concentration of 6 mg/ 1 mL.

Magnetic functionalization of Au microplates

To render the Au microplates magnetic, 25-500 µL of the aqueous ferrofluid solution was added to 12 mL of DI H_2O; the solution was mixed and sonicated for 5 min. Next, 500 µL of the Au plate solution was

added and the combined solution was shaken and sonicated for 30 minutes to ensure the adsorption of the magnetic particles onto the Au surface. Afterwards, the solution was centrifuged and decanted, and the magnetized microplates were suspended in 1 mL of DI H_2O for use in performance studies.

Microscopy and photography

Transmission electron microscopy (TEM) was performed using a Philips Technai 12 operated at 120 kV; all TEM samples were prepared via dropcasting. Scanning electron microscopy (SEM) was performed using a Philips XL30 FEG instrument; samples were dropcast on Si wafers. Optical microscopy was performed using a Zeiss Axio Imager A1m. Microplate samples for optical imaging were prepared by diluting a magnetized plate sample 15 times in DI H_2O, then mixing 120 µL of the diluted sample with 5 µL of aqueous agarose solution (0.5 wt %, stored at 70 °C); the agarose served to enhance the colloidal stability of the microplates and prevent their irreversible adhesion to the capillary walls via steric repulsion.[5] The plate sample was then added into a 0.4 mm flat glass capillary (EMS); both ends were sealed using optical glue. The microplates were then rotated by placing a ~ 2300 G (field strength at magnet surface) circular rare earth magnet near the sample and varying its orientation. For photographs of the plates in bulk, the microplate solution was injected into a 3 mm path length homemade cuvette; the cuvettes were made by placing a rubber plumbing O-ring between two glass slides and gluing them together using epoxy. After the epoxy was cured, the sample could be conveniently injected into the cuvette by piercing the rubber O-ring with a hypodermic needle. Plates were rotated using a larger ~ 2900 G circular rare earth magnet at a center-center distance of ~ 5 cm.

Transmittance and reflectance measurements

Optical transmittance and reflectance measurements were taken using an Ocean Optics DH-2000-BAL UV-Vis spectrophotometer using the respective attachments. For transmittance measurements, the microplate solution was placed in a sealed 1 mm thick flat glass capillary (EMS). A ~ 2900 G circular

magnet was placed ~ 8.5 cm (center-center distance) beneath the sample and rotated to change the microplate orientation relative to the beam path. For reflectance measurements, the conditions were similar except a 3 mm path length cuvette was used.

Optical modulation measurements

Optical modulation measurements were conducted by passing a 635 nm laser through a 3 mm cuvette containing microplate samples with varying magnetic loading. The microplate sample was manipulated using a standard magnetic stir plate operating at 240 rpm, or 4 Hz, which generated a ~20 mT rotating magnetic field to actuate the microplates in a circular fashion, causing the sample to "blink" rapidly. The transmitted intensity was measured via a photodetector connected to an oscilloscope, which recorded the optical modulation over a set time period. For each complete rotation of the stir plate magnet, the microplates underwent two cycles of oscillation.

References

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