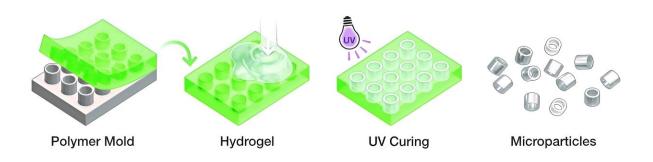


Ultra-small, shape-shifting GEMS offer an easier and cheaper way to improve MRI imaging

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A hard silicon master mold is used to create a flexible polymer mold, which is flipped over and filled with hydrogel. The hydrogel is then cured with UV light, producing the cylindrical microparticles. Credit: S. Kelley/NIST

Microscopic magnetic probes that change shape in response to their environment may greatly enhance magnetic resonance imaging (MRI). However, producing the probes, which are still experimental and have not yet been used in humans, has required access to a clean room and expertise in nanofabrication, limiting their widespread use.

Now, researchers at the National Institute of Standards and Technology (NIST) have taken these shape-shifting probes, known as geometrically encoded <u>magnetic sensors</u>, or GEMS, a step further by unveiling a novel

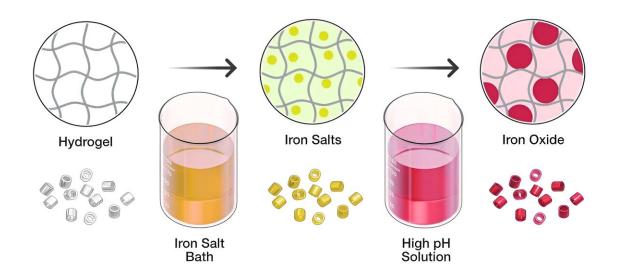


fabrication method that is not only faster and cheaper but eliminates the need for specialized instruments.

The scientists reported their work online Dec. 19 in ACS Sensors.

Instead of building the tiny probes layer by layer in a nanofabrication facility, the team constructed them using a precision master mold. This technique allows researchers to make GEMS in their own laboratories using inexpensive materials and readily available equipment.

NIST scientists Gary Zabow and Samuel Oberdick and their colleagues focused their efforts on building GEMS shaped like tiny hollow cylinders because that shape can be easily fabricated with a mold. For their master mold, the scientists constructed an array of hollow cylinders made of hard silicon, each only about 100 micrometers in diameter—about ten times larger than a red blood cell.



The microparticles are soaked in a bath of iron salts, permeating the hydrogel with iron salts. They are then transferred to a high pH solution, which transforms



the iron salts in the hydrogel into magnetic iron oxide particles. Credit: S. Kelley/NIST

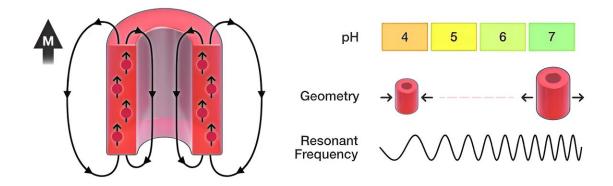
The team then demonstrated how researchers with such a master mold could complete the multi-step fabrication process. First, the scientists made a soft-mold "negative" of the master by pouring a liquid polymer on top of the hard silicon mold, allowing it to solidify, and then peeling it off. This created a pliable mold with an array of cylindrical hollow cavities.

In the next step, the scientists filled each cavity with a liquid precursor to a hydrogel—a network of cross-linked polymers that can absorb large amounts of water. The hydrogel, which had been engineered to shrink or swell in response to changes in acidity or other properties in its microenvironment, is a key component of the GEMS. Engineered hydrogels are inexpensive and easy to make.

After hardening the hydrogels by exposing them to <u>ultraviolet light</u>, the NIST team turned them out of their soft mold, similar to popping icecubes out of a silicon tray. The cylindrical hydrogels were then immersed in a bath of iron salts and transferred to a basic solution, which converted the iron salts absorbed by the hydrogels into magnetic oxide particles.

The strength of each <u>hydrogel</u>'s <u>magnetic field</u> has a direct bearing on MRI, which manipulates the tiny magnetic fields of protons to image internal structures in the human body. Protons behave like spinning magnetized tops, each initially pointing in a random direction.





When placed in a strong external magnetic field (labeled M), the iron oxide particles become magnetized, causing the microparticles to develop their own local magnetic field. The microparticles shrink and swell with changes in acidity, which strengthens or weakens this local field and therefore how much the field influences the resonant frequency of protons during an MRI scan. Credit: S. Kelley/NIST

An MRI machine aligns the magnetic field of the protons with its own strong magnetic field and then disrupts that alignment by tickling the protons with a pulse of radio waves at a resonance frequency that causes the protons to alternately "relax" into their original states and then become aligned again. As the protons cycle back and forth between the two states, they emit <u>radio waves</u>, which are translated into MRI images.

Meanwhile, the <u>hydrogels</u> change their shape in response to changes in local conditions, and as a result their magnetic field strengthens or weakens.

The changing magnetic field of the GEMS shifts the <u>resonance</u> <u>frequency</u> of the protons that lie in or near the probes. By measuring the shift, MRI can detect how the GEMS have altered their shape in response to a specific property in their local environment.



GEMS that are built with the soft-mold process can be tailored to change their shape to a host of environmental properties, allowing researchers to use the probes to explore a range of biomedical conditions, Oberdick said.

More information: Samuel D. Oberdick et al, Shaped Magnetogel Microparticles for Multispectral Magnetic Resonance Contrast and Sensing, *ACS Sensors* (2023). DOI: 10.1021/acssensors.3c01373

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