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ACS central science

CENTER STAGE

In collaboration with **C&EN**

A Conversation with Serena Corr

Mark Peplow

This materials scientist is helping preserve the iconic warship *Mary Rose*, once part of King Henry VIII's navy.

n July 19, 1545, King Henry VIII of England watched in dismay as one of his greatest warships, the Mary Rose, sank during the Battle of the Solent in the strait between Britain's south coast and the Isle of Wight, taking the lives of hundreds of sailors with it. The English fleet eventually won its battle against the French, but the Mary Rose remained on the seabed for centuries. Then, in 1982, the oak vessel was raised in a spectacular feat of underwater archeology. The ship and its artifacts are now kept at the Mary Rose museum in Portsmouth, England, but conservators now face a battle of their ownpreserving the ship's oak timbers from decay. At the American Chemical Society national meeting in August, Serena Corr of the University of Sheffield explained how she is using nanotechnology to help save the Mary Rose. Mark Peplow caught up with Corr to get the latest on the project.

Why is the ship's hull degrading?

Over many hundreds of years, while the ship was on the seabed, various metal fixtures eroded and left iron residues in the wood. You also have sulfur-reducing bacteria in the marine environment that penetrated the wood, bringing sulfur with them. Iron and sulfur react to form iron sulfides, which are perfectly happy in seawater. But in an oxygen environment, when the ship is out of the water, they start to form harmful acids like sulfuric acid that damage the wood.

How did you get involved in tackling the problem?

It started about three years ago. I was chatting with my friend Eleanor Schofield, who is a professor at the Mary Rose museum and is responsible for exploring new conservation treatments. She'd been looking at things like strontium carbonate nanoparticles, which combine with sulfur compounds to form unreactive strontium sulfate. The nanoparticles also react with iron to form iron carbonate



Credit: Stuart Campbell/University of Glasgow

residues, which remain on the wood surface and change its appearance. It would be advantageous to completely remove iron ions from the wood, preferably with a treatment that is easy to apply and remove without causing any damage.

At the time, I was working on iron oxide magnetic nanoparticles that could be used in magnetic resonance imaging. We thought we could coat the nanoparticles with some agent that captures the iron in the ship's timbers. We could use an external magnetic field to drive these nanocomposites into the wood, and then remove them magnetically along with the iron. It's intended to treat spots on the hull where you clearly have a lot of iron bleeding out of the wood.

What's the chemistry behind your method?

It's based on nanoparticles of magnetite (Fe_3O_4) about 10 nm across, with porphyrin molecules on the surface that bind to iron ions in the wood. The particle size is very important because it means the particles take on properties that are quite different from their bulk counterparts—they become superparamagnetic, meaning that an external

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magnetic field can easily magnetize them. The practical outcome is that these particles act as individual little magnets that repel each other, so they don't tend to cluster together into large aggregates. That is very important when you want to try and drive these particles into the channels present in wood.

We also needed to apply these nanoparticles to the wood and remove them again without causing any damage to the ship. So I talked to Rachel O'Reilly at the University of Birmingham, who had been working on these really interesting thermoresponsive polymer gels.

First, we apply a polymer gel containing the functionalized nanoparticles to the surface of the wood. When we reduce the temperature by a degree or two, the gel transforms into a liquid and releases the particles. Then we use an everyday rare-earth magnet to drive the particles into the wood, where they stay for an incubation period and bind to free iron ions. After that, we apply a magnetic field to pull the particles out of the wood with their iron cargo and then raise the temperature just enough to turn the liquid back into a gel again. That makes it very easy to peel the gel off the surface of the wood. It's sort of a face mask for the *Mary Rose*.

Have you tested this on the ship yet?

We first did a huge number of test treatments on fresh oak samples that had been soaked in iron solution to show that the gel-particle mixture works. We've just started tests on actual *Mary Rose* timbers, and I'm really excited about it. It'll take about a month before we have any results, but we are quite hopeful. We've done absorption tomography experiments on *Mary Rose* oak, and we see that it's a lot more degraded compared to fresh oak, so it should be much easier for our nanoparticles to penetrate.

How do you actually make the nanoparticles?

We've developed some microwave chemistry to make the nanoparticles. The heating is very even, so we get nanoparticles of a very uniform size in gram-scale quantities. Some other methods for making iron oxide nanoparticles require organic solvents, but this allows us to prepare the particles in an aqueous medium, which we require for the *Mary Rose* work. We chemically attach the porphyrin molecules via a linker on the surface of the nanoparticles. The whole synthesis is quite cheap, which is an important consideration for museums where budgets might be constrained.

Could this approach be applied to other conservation challenges?

Absolutely. Over 19,000 artifacts were also recovered from the *Mary Rose*, and many of those require various levels of treatment. We've started doing experiments on samples of leather, rope, and sailcloth to understand the degradation processes in these artifacts. Each material may require a different type of treatment, and what's really nice about this magnetic nanoparticle approach is that the chemistry is quite tunable. The porphyrin works really well for removing iron, but we could attach different molecules to bind other ions.

Even though most of my research is on functional materials with energy and environmental applications, like battery electrodes, it has been one of the greatest privileges of my career to work on the *Mary Rose* and to play a small role in conserving her.

Mark Peplow is a freelance contributor to Chemical & Engineering News, the weekly newsmagazine of the American Chemical Society. Center Stage interviews are edited for length and clarity.