Bringing salvaged wooden ships and artifacts back to life with 'smart' nanotech

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Thousands of shipwrecks litter the seafloor all over the world, preserved in sediments and cold water. But when one of these ships is brought up from the depths, the wood quickly starts deteriorating. Today, scientists report a new way to use "smart" nanocomposites to conserve a 16th-century British warship, the *Mary Rose*, and its artifacts. The new approach could help preserve other salvaged ships by eliminating harmful acids without damaging the wooden structures themselves.

The researchers are presenting their results today at the 256th National Meeting & Exposition of the American Chemical Society (ACS).

"This project began over a glass of wine with Eleanor Schofield, Ph.D., who is head of conservation at the Mary Rose Trust," recalls Serena Corr, Ph.D., the project's principal investigator. "She was working on techniques to preserve the wood hull and assorted artifacts and needed a way to direct the treatment into the wood. We had been working with functional magnetic nanomaterials for applications in imaging, and we thought we might be able to apply this technology to the *Mary Rose*."

The *Mary Rose* sank in 1545 off the south coast of England and remained under the seabed until she was salvaged in 1982, along with over 19,000 artifacts and pieces of timber. About 40 percent of the original structure survived. The ship and its artifacts give unique insights into Tudor seafaring and what it was like to live during that period. A state-of-the-art museum in Portsmouth, England, displays the ship's hull and artifacts.

While buried in the seabed, sulfur-reducing marine bacteria migrated into the wood of the *Mary Rose* and produced hydrogen sulfide. This gas reacted with iron ions from corroded fixtures like cannons to form iron sulfides. Although stable in low-oxygen environments, sulfur rapidly oxidizes in regular air in the presence of iron to form destructive acids. Corr's goal was to avoid acid production by removing the free iron ions.

Once raised from the seabed, the ship was sprayed with cold water, which stopped it from drying out and prevented further microbial activity. The conservation team then sprayed the hull with different types of polyethylene glycol (PEG), a common polymer with a wide range of applications, to replace the water in the cellular structure of the wood and strengthen its outer layer.

Corr and her postdoctoral fellow Esther Rani Aluri, Ph.D., and Ph.D. candidate Enrique Sanchez at the University of Glasgow are devising a new family of tiny magnetic nanoparticles to aid in this process, in collaboration with Schofield and Rachel O'Reilly, Ph.D., at the University of Warwick. In their initial step, the team, led by Schofield, used synchrotron techniques to probe the nature of the sulfur species before turning the PEG sprays off, and then periodically as the ship dried. This was the first real-time experiment to closely examine the evolution of oxidized sulfur and iron species. This accomplishment has informed efforts to design new targeted treatments for the removal of these harmful species from the *Mary Rose* wood.

The next step will be to use a nanocomposite based on core magnetic iron oxide nanoparticles that include agents on their surfaces that can remove the ions. The nanoparticles can be directly applied to the porous wood structure and guided to particular areas of the wood using external magnetic fields, a technique previously demonstrated for drug delivery. The nanocomposite will be encompassed in a heat-responsive polymer that protects the nanoparticles and provides a way to safely deliver them to and from the wood surface. A major advantage of this approach is that it allows for the complete removal of free iron and sulfate ions from the wood, and these nanocomposites can be tuned by tweaking their surfaces.

With this understanding, Corr notes, "Conservators will have, for the first time, a state-of-the-art quantitative and restorative method for the safe and rapid treatment of wooden artifacts. We plan to then transfer this technology to other materials recovered from the *Mary Rose*, such as textiles and leather."

More information: Magnetic nanocomposite materials for the archeological waterlogged wood conservation, the 256th National Meeting & Exposition of the American Chemical Society (ACS).

Abstract
The 16th century English warship, Mary Rose, sank off the south coast of England and remained under the seabed for 437 years until she was salvaged in 1982. The conservation of her waterlogged wooden artefacts is of enormous importance, as it gives us a unique insight into Tudor history. However, this is an immense challenge due to the nature of degradation of the wooden hull which is driven by biologically, chemically, and mechanically induced changes from long-term exposure to the marine environment. To lend structural stability to the hull, she has been sprayed with solutions of polyethylene glycol (PEG-200 and PEG-2000) for 30 years, before a drying phase commenced. Besides facing structural integrity issues, the deposition of iron and sulfur-based species within the Mary Rose timbers whilst under the seabed are generating harmful acids within the wood structure. These arise from dissolution of iron fixture aboard the ship and the activity of sulfur-reducing marine bacteria. X-ray absorption near-edge spectroscopy (XANES) studies reveal the existence of a variety of sulfur- and iron-based species along the core wood and a high content of oxidized sulfur

on wood surface. Having these insights are crucial to determining appropriate and targeted treatment strategies for the removal of these harmful chemicals. Our group is designing a range of tunable nanostructures based on functionalized magnetic nanoparticles as conservation platforms to target and remove this harmful iron and sulfur entities lodged inside the wood. The magnetic nature of the composite allows for removal via the application of an external magnetic field. These magnetic nanoparticles are also functionalized with thermo-reversible PEG methacrylate polymer gels to allow easy application and removal from the Mary Rose wood. These nanocomposites have been tested as sequestering agents for iron in fresh and aged oak samples. I will present our latest results on these efforts, as well as an overview of the use of XANES for studying the Mary Rose. This is the first time such an approach has been taken to treat the Mary Rose wooden hull and its tunability means it could be employed to preserve a range of artefacts recovered from the Mary Rose site.

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