How a Virus Earned Its Nanorod-synthesizing Stripes

Being able to synthesize nanomaterials with controllable dimensions remains an important challenge in nanotechnology. Toward that end, some research teams have looked at utilizing naturally occurring biomaterials, such as viruses, as templates to reliably produce predictable nanostructures on a large scale. Thus far, the majority of studies in this area have focused on just two viruses: the M13 bacteriophage and the tobacco mosaic virus (TMV). Taking advantage of the multiple functionalities afforded by these viruses' protein coats, such as polar, hydrophilic, charged, acidic, and basic chemical groups, researchers have been able to create an array of nanostructures by coating these viruses with noble metals, bimetallic materials, and semiconductors. However, these viruses are just two in a vast multitude of virus species on the planet. In an effort to expand the biodiversity of virus templates, a team of researchers tested the potential of the barley stripe mosaic virus (BSMV) to produce metallic nanomaterials. Coating this virus with the noble metal palladium (Pd), the researchers found that BSMV could readily template the production of high-quality nanorods. A variety of synchrotron x-ray experiments carried out at the APS allowed the researchers to characterize both the mineralization process and the structures of particles as they developed. The findings showcase the potential of BSMV for nanomaterial synthesis.

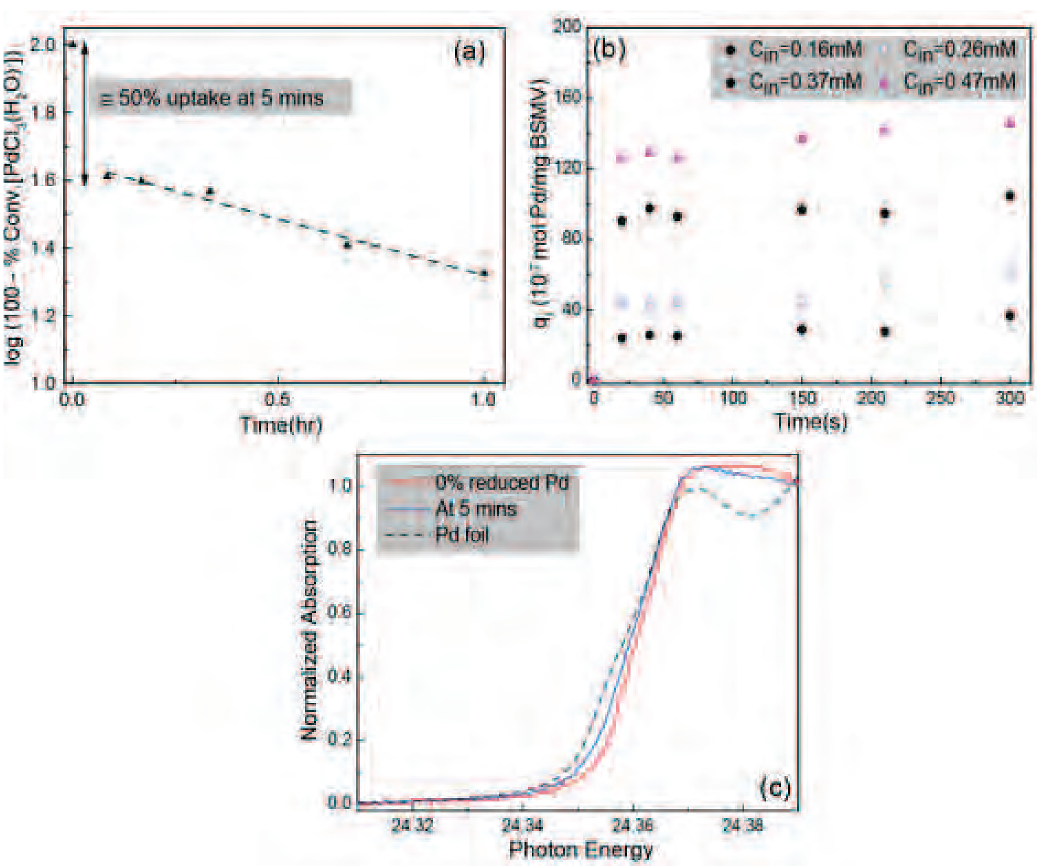

Fig. 1. Changes in Pd during mineralization on BSMV. (a) First order kinetic model fit to $[PdCl_3(H_2O)]^-$ uptake on BSMV (b) Uptake of $PdCl_3(H_2O)^-$ at early times obtained by UV-Vis absorbance experiments at 256 nm. (c) XANES spectra of Pd references and spectrum at five minutes after incubation. Experiments were performed at six different $Pd^{(2+)}$ concentrations (three of them are shown here).

9-ID-B,C • XSD • Chemistry, materials science, life sciences • Nanoimaging, microfluorescence (hard x-ray), coherent x-ray scattering (hard x-ray), ultra-small-angle x-ray scattering • 4.5-30 keV • On-site • Accepting general users •

10-ID-B • MR-CAT • Materials science, environmental science, chemistry • X-ray absorption fine structure, time-resolved x-ray absorption fine structure, microfluorescence (hard x-ray) • 4.3-27 keV, 4.8-32 keV, 15-65 keV • On-site • Accepting general users •

To determine this virus' suitability as a biotemplate, the researchers from Purdue University started by adding a solution containing BSMV to a continuous stirred-tank reactor containing a Na_2PdCl_4 solution. After a 20-min incubation, transmission microscopy images showed the formation of nanorods on the viral coat. The BSMV was coated with palladium nanoparticles, which had an initial diameter of 1 to 2 nm. After recoating the BSMV several times, the diameter of the Pd-coated BSMV increased to about 57 nm.

Sampling the reaction materials periodically during the incubation process, the researchers used UV-vis spectroscopy and x-ray absorption spectroscopy to characterize the biomineralization process (Fig. 1). Their findings showed that Pd from the Na_2PdCl_4 solution adsorbed to the viruses within seconds after combination, a process driven by both electrostatic and covalent bonds between the precursor Pd ions and the functional groups on the viral coat. The total absorption capacity of BSMV proved to be more than double that of TMV under the same reaction conditions.

After several minutes, the adsorbed Pd ions then underwent a reduction reaction, a process, which lasted up to several hours. Further coatings repeated this process, sequentially thickening the diameter of the nanorods (Fig. 2).

Further investigation by the Purdue team and Argonne colleagues utilizing x-ray absorption spectroscopy (XAS) and small- (SAXS) and ultra-small-angle x-ray scattering (USAXS) at the XSD 9-ID-B,C and MR-CAT 10-ID-B beamlines at the APS (SAXS/USAXS at 9-ID-B,C and *in situ* XAS at 10-ID-B) showed that these particles displayed a core-shell morphology and were uniform and monodisperse, with quality as high as those synthesized using TMV as a biotemplate. Because the x-ray imaging techniques allowed the researchers to follow growth from the primary Pd nanoparticles through their growth to final size, the researchers note that to their knowledge, this study is the first to comprehensively and simultaneously analyze all size levels in a rod-like mineralized virus.

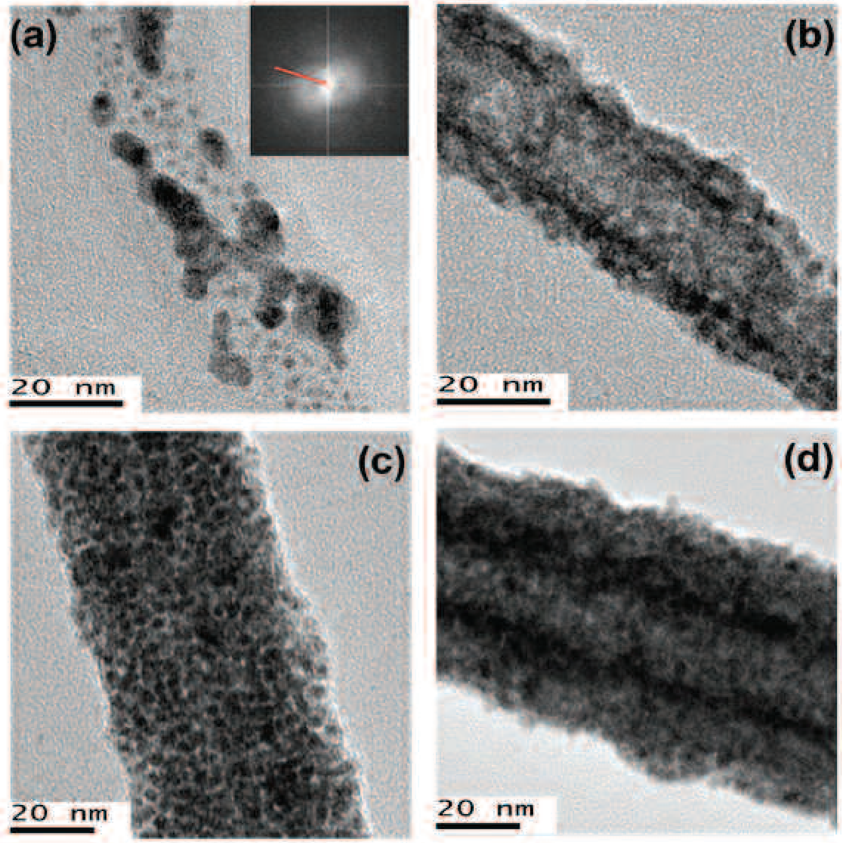

Fig. 2. TEM images of single BSMV-Pd after incubation of 0.02 mg/mL of BSMV in 7.5 × 10^{-2} mM of Na_2PdCl_4. BSMV-Pd collected after (a) one coating cycle. Inset in shows the Fourier transform of a high-resolution TEM (HRTEM) image of Pd particles after one coating. Spacing 0.22 nm corresponding to d(111) of $Pd^{(0)}$ was observed (b) two coating cycles (c) BSMV-Pd collected after five coating cycles and (d) six coating cycles.

They add that in total, these findings expand the biotemplate toolbox for synthesizing new materials and comparatively studying biomineralization processes between templates. The unique active surface of these particles left on the viral coat could serve in a variety of applications, the researchers say, such as catalysis, battery electrodes, and further electroless deposition. In addition, this work shows that the native amino acid and functional groups on BSMV offer the potential of new kinds of mineralization possibilities not yet realized with current biotemplate offerings.

Future research might be able to expand the products of these synthesis reactions by genetic engineering of the virus, metallization with other metals, and exploring selective inner channel mineralization to produce superfine nanowires. *— Christen Brownlee*

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