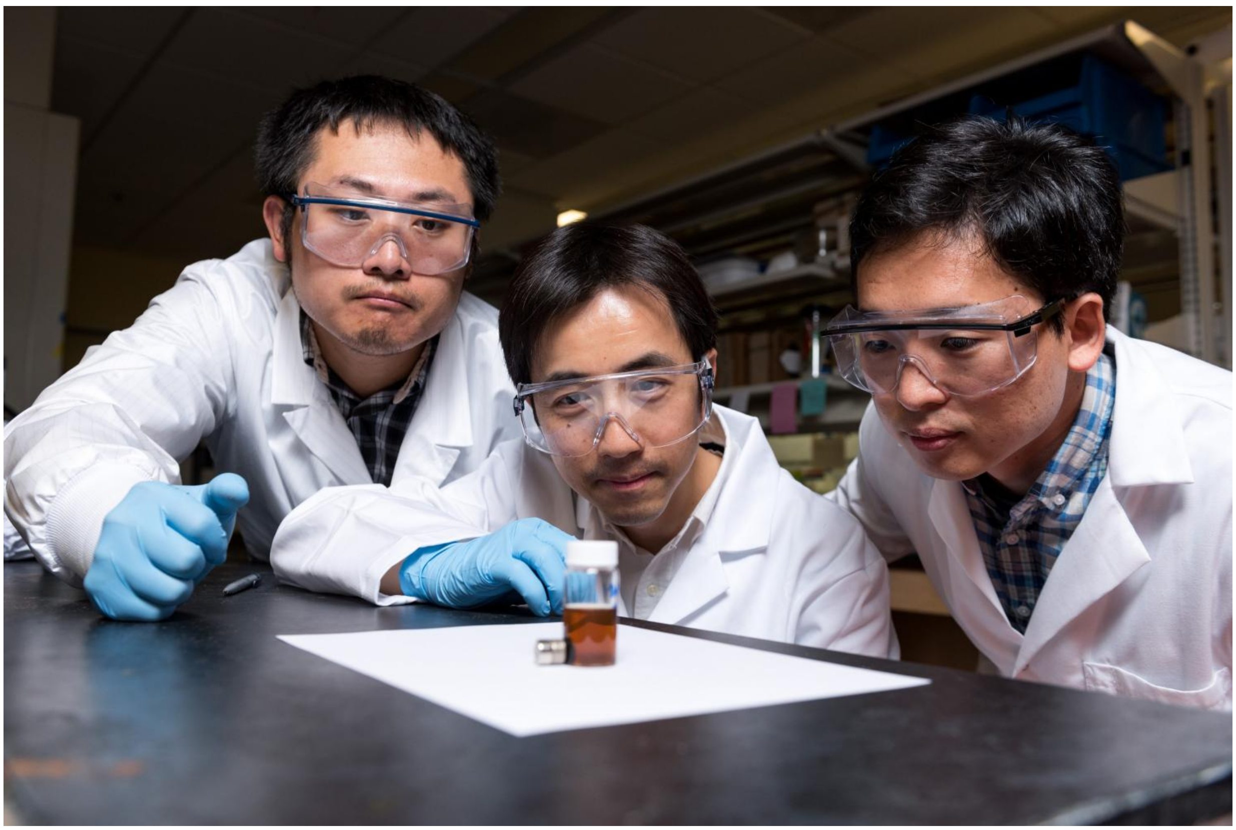
Uniform 'hairy' nanorods have potential energy, biomedical applications

September 15 2016, by John Toon



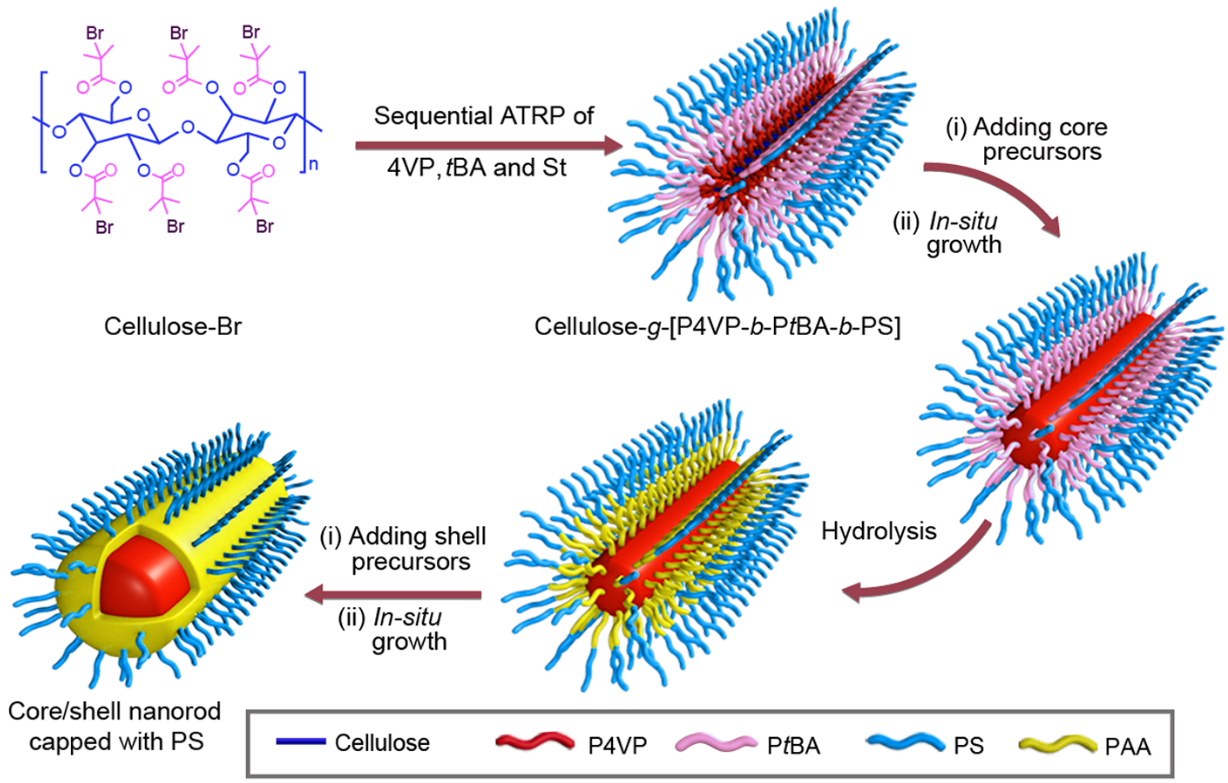
Georgia Tech researchers (left to right) Yanjie He, Zhiqun Lin, and Jaehan Jung demonstrate how magnetic nanorods in the vial are attracted to a magnet held near the vial. The researchers have developed a new strategy for crafting one-dimensional nanorods based on cellulose using a wide range of precursor materials. Credit: Rob Felt, Georgia Tech

Materials scientists have developed a new strategy for crafting one-dimensional nanorods from a wide range of precursor materials. Based on a cellulose backbone, the system relies on the growth of block copolymer "arms" that help create a compartment to serve as a nanometer-scale chemical reactor. The outer blocks of the arms prevent aggregation of the nanorods.

The produced structures resemble tiny bottlebrushes with polymer "hairs" on the nanorod surface. The nanorods range in size from a few hundred nanometers to a few micrometers in length, and a few tens of nanometers in diameter. This new technique enables tight control over diameter, length and surface properties of the nanorods, whose optical, electrical, magnetic and catalytic properties depend on the precursor materials used and the dimensions of the nanorods.

The nanorods could have applications in such areas as electronics, sensory devices, energy conversion and storage, drug delivery, and cancer treatment. Using their technique, the researchers have so far fabricated uniform metallic, ferroelectric, upconversion, semiconducting and thermoelectric nanocrystals, as well as combinations thereof. The research, supported by Air Force Office of Scientific Research, was reported in the September 16 issue of the journal *Science*.

"We have developed a very general and robust strategy to craft a rich variety of nanorods with precisely-controlled dimensions, compositions, architectures and surface chemistries," said Zhiqun Lin, a professor in the School of Materials Science and Engineering at the Georgia Institute of Technology. "To create these structures, we used nonlinear bottlebrush-like block copolymers as tiny reactors to template the growth of an exciting variety of inorganic nanorods."

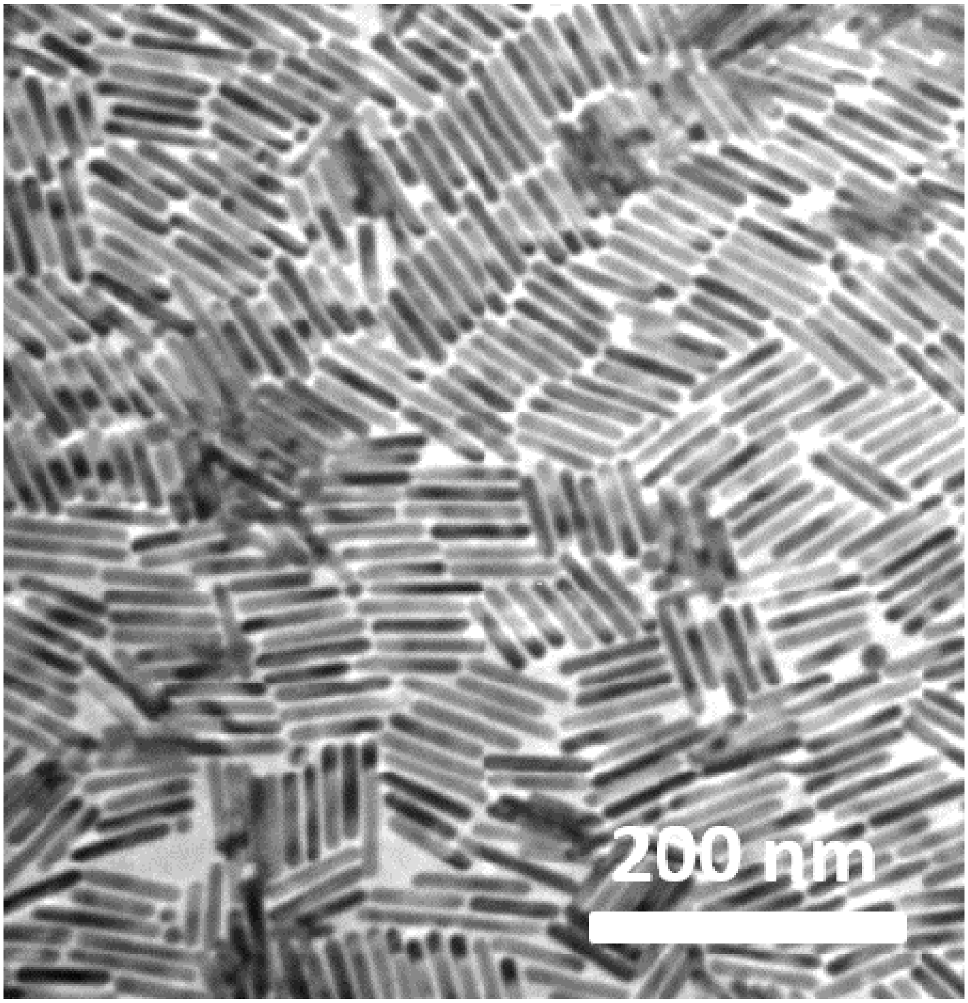


Schematic shows the steps involved in producing oil-soluble core-shell nanorods capped with polystyrene. Credit: Georgia Tech

Nanorod structures aren't new, but the technique used by Lin's lab produces nanorods of uniform sizes – such as barium titanate and iron oxide, which have not yet been demonstrated via wet-chemistry approaches in the literature – and highly-uniform core-shell nanorods made by combining two dissimilar materials. Lin and former postdoctoral research associate Xinchang Pang say the precursor materials applicable to the technique are virtually limitless.

"There are many precursors of different materials available that can be used with this robust system," Lin said. "By choosing a different outer block in the bottlebrush-like block copolymers, our nanorods can be dissolved and uniformly dispersed in organic solvents such as toluene or chloroform, or in water."

Fabrication of the nanorods begins with the functionalization of individual lengths of cellulose, an inexpensive long-chain biopolymer harvested from trees. Each unit of cellulose has three hydroxyl groups, which are chemically modified with a bromine atom. The brominated cellulose then serves as macroinitiator for the growth of the block copolymer arms with well-controlled lengths using the atom transfer radical polymerization (ATRP) process, with, for example, poly(acrylic acid)-block-polystyrene (PAA-b-PS) yielding cellulose densely grafted with PAA-b-PS (i.e., cellulose-g-[PAA-b-PS]) that give the bottlebrush appearance.



Transmission electron microscope image shows lead telluride (PbTe) nanorods developed by materials scientists at the Georgia Institute of Technology using a new strategy for crafting one-dimensional nanorods from a wide range of precursor materials. Credit: Georgia Tech

The next step involves the preferential partitioning of precursors in the inner PAA compartment that serves as a nanoreactor to initiate the nucleation and growth of nanorods. The densely grafted block copolymer arms, together with the rigid cellulose backbone, give researchers the ability to not only prevent aggregation of the resulting nanorods, but also to keep them from bending.

"The polymers are like long spaghetti and they want to coil up," Lin explained. "But they cannot do this in the complex macromolecules we make because with so many block copolymer arms formed, there is no space. This leads to the stretching of the arms, forming a very rigid structure."

By varying the chemistry and the number of blocks in the arms of the bottlebrush-like block copolymers, Lin and coworkers produced an array of oil-soluble and water-soluble plain nanorods, core-shell nanorods, and hollow nanorods – nanotubes – of different dimensions and compositions.

Image shows magnetic nanorods in the vial attracted to the magnet. Georgia Tech researchers have developed a new strategy for crafting one-dimensional nanorods based on cellulose using a wide range of precursor materials. Credit: Rob Felt, Georgia Tech

For example, by using bottlebrush-like triblock copolymers containing densely grafted amphiphilic triblock copolymer arms, the core-shell nanorods can be formed from two different materials. In most cases, a large lattice mismatch between core and shell materials would prevent the formation of high-quality core-shell structures, but the technique overcomes that limitation.

"By using this approach, we can grow the core and shell materials independently in their respective nanoreactors," Lin said. "This allows us to bypass the requirement for matching the crystal lattices and permits fabrication of a large variety of core-shell structures with different combinations that would otherwise be very challenging to obtain."

Lin sees many potential applications for the nanorods.

Image shows a vial containing water-soluble gold nanorods. Georgia Tech researchers have developed a new strategy for crafting one-dimensional nanorods based on cellulose using a wide range of precursor materials. Credit: Rob Felt, Georgia Tech

"With a broad range of physical properties – optical, electrical, optoelectronic, catalytic, magnetic, and sensing – that are dependent sensitively on their size and shape as well as their assemblies, the produced nanorods are of both fundamental and practical interest," Lin said. "Potential applications include optics, electronics, photonics, magnetic technologies, sensory materials and devices, lightweight structural materials, catalysis, drug delivery, and bio-nanotechnology."

For example, plain gold nanorods of different lengths may allow effective plasmonic absorption in the near-infrared range for use in solar energy conversion with improved harvesting of solar spectrum. The upconversion nanorods can preferentially harvest the IR solar photons, followed by the absorption of emitted high-energy photons to generate extra photocurrent in solar cells. They can also be used for biological labeling because of their low toxicity, chemical stability, and intense luminescence when excited by near-IR radiation, which can penetrate tissue much better than higher energy radiation such as ultraviolet, as is often required with quantum dot labels.

The gold-iron oxide core-shell nanorods may be useful in cancer therapy, with MRI imaging enabled by the iron oxide shell, and local heating created by the photothermal effect on the gold nanorod core killing cancer cells.

More information: Xinchang Pang, Yanjie He, Jaehan Jung, Zhiqun Lin, "1D nanocrystals with precisely controlled dimensions, compositions, and architectures," *Science* 2016. science.sciencemag.org/cgi/doi … 1126/science.aad8279

Provided by Georgia Institute of Technology