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News and opinions

3D printing makes piezoelectrics smart

Cordelia Sealy

A radical new approach could make it possible to print multi-functional impact or force sensors from piezoelectric nanoparticle inks, which could be easily incorporated into wearable devices, clothing or other items [Cui et al., *Nature Materials* 18 (2019) 234-241, https://doi.org/10.1038/s41563-018-0268-1].

Piezoelectric materials transform mechanical work into electrical energy and vice versa, so have wide-ranging applications from pressure sensing and actuation to energy harvesting. But the conversion abilities of piezoelectric ceramics and composites are dictated by their intrinsic composition and crystal structure.

Now, however, researchers from Virginia Tech and Pennsylvania State University have found a means of getting around the limitations of crystal structure by using 3D printing to construct piezoelectric nanocomposites with complex architectures and tunable responses to applied stress. These designer piezoelectric metamaterials achieve higher specific piezoelectric constants than their parent materials at a fraction of the weight while maintaining a high degree of flexibility (Fig. 1a and b).

"This study, for the first time, realizes the design of arbitrary piezoelectric properties by creating 3D lattices that mimic but alter the intrinsic crystal orientations of piezoelectric materials," says Xiaoyu (Rayne) Zheng, who led the research at Virginia Tech. "Unlike conventional piezoelectrics where electric charge movements are prescribed by the intrinsic crystal structure, the new method allows users to prescribe and program voltage responses to be magnified, reversed, or suppressed in any direction."

The building blocks of these versatile smart materials are functionalized lead zirconate titanate (PZT) nanoparticle colloids, which are covalently bonded with ultraviolet-sensitive photoactive monomers. In effect, the photosensitized nanoparticle colloids act as a piezoelectric ink that can be printed into highly complex, free-form 3D architectures using a high-resolution digital 3D printer.

"We developed a digital light-projection-based 3D printing technique to process these highly viscous, piezoelectric nanocrystal colloids," explains Zheng.

The approach can be applied to materials other than PZT, point out the researchers. A wide range of piezoelectrics, including barium titanate (BTO), could be functionalized in this way, as well as other materials such as the multiferroic bismuth ferrite.

"The resulting materials unleash piezoelectric material design opportunities that have never been seen before, enabling the creation of piezoelectric materials from soft and flexible to rigid and energy absorbing," he says, "resulting in intelligent, structural materials that can perform self-sensing and diagnostics without having to use any sensors."

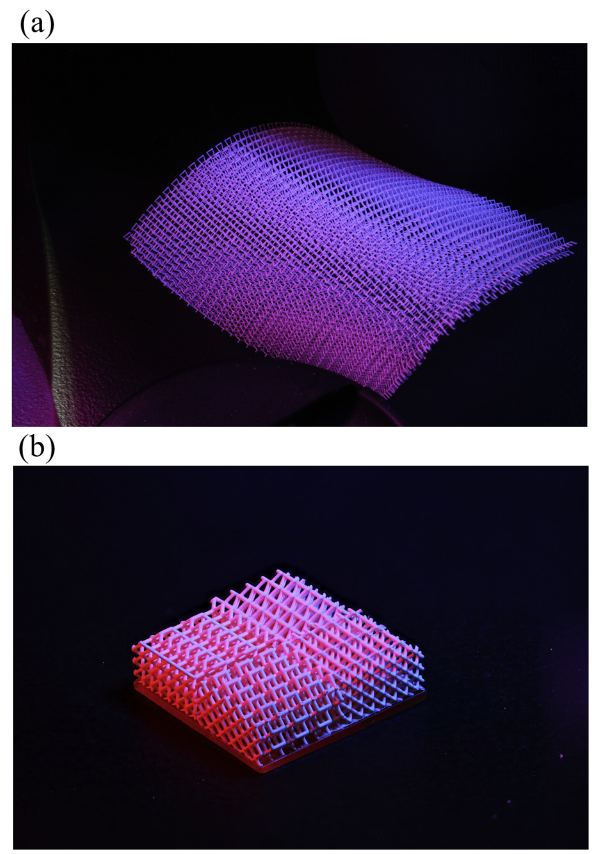

Fig. 1. (a) A printed flexible sheet of piezoelectric smart material. (Photo courtesy of H. Cui, Zheng Lab.) (b) An assembled smart piezo-active structural sensor.

These adaptable piezoelectric composites could form the basis of a next generation of intelligent devices performing a range of structural and functional tasks from impact absorption and detection to three-dimensional pressure mapping.

"By programming the 3D active topology, you can achieve pretty much any combination of piezoelectric coefficients within a material and use them as transducers or sensors that are not only flexible and strong, but also respond to pressure, vibrations, and impacts via electric signals that tell the location, magnitude, and direction of impacts anywhere within the material," points out Zheng.

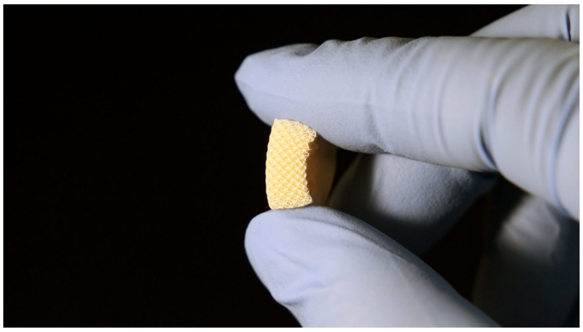

Fig. 2. 3D printed, flexible energy harvester. (Photo courtesy of H. Cui, Zheng Lab.)

He is confident that the approach will allow engineers to custom design and print transducers and flexible energy harvesting devices without the need for expensive cleanroom facilities (Fig. 2). The researchers are now working on improving the process so that fully functional devices can be fabricated using a desktop printer.

Zhong Lin Wang of Georgia Tech, one of the pioneers of piezoelectric technology, comments:

"This paper introduces 3D printing to fabricate piezoelectric materials with designed anisotropy and directional response. This is a new approach toward building multiple function sensors using composites of piezoelectric materials in any shape or even any dimension."

He believes the work will be important for guiding sensor systems for soft robotics, intelligent actuators, and new mechanical triggering structures.

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New nanotube comes with built-in holes

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Researchers have synthesized a new type of carbon-based nanotube using benzene rings as building blocks [Sun et al., *Science* **363** (2019) 151–155, https://doi.org/10.1126/science.aau5441]. Instead of carbon atoms in a regular carbon nanotube, the new chemical structure is composed of hexagonal six-membered benzene rings. Because of the way in which the rings bond together, the resulting cylinder contains regular defects in the form of gaps or holes. If many of these cylindrical molecules could be linked together, the resulting carbon nanotubes would have properties defined by these vacancies.

The team from the University of Tokyo, Japan Science and Technology Agency (JST), Center for Emergent Matter Science at RIKEN, and Tohoku University synthesized the phenine nanotube (pNT) molecules, which have the chemical formula $C_{304}H_{264}$, in a nine-step process. Despite the complexity of the multi-step process, it is relatively efficient say the researchers.

"The benzene rings are synthetically stitched together by 52 covalent bonds with a high average efficiency of 91%," explains Hiroyuki Isobe of the University of Tokyo, who led the study.

The process begins with six molecules of benzene, which are combined into a larger ring called cyclo-meta-phenylene (CMP). In the presence of Pt, four CMP molecules form an open-ended cube. When the Pt atoms are removed, the cube closes up to form a cylinder (Fig. 1). The resulting pNT molecule is just 2 nm in size.

"From a chemistry perspective, our demonstration of concise synthesis of a large rigid cylinder is novel," says Isobe. "We believe no one had ever imagined that one could synthesize a 2-nm $C_{304}H_{264}$ molecule with a molecular weight of 4 kDa from benzene in nine steps."

The molecules themselves are uniquely interesting, but they can also be fused together to form highly porous nanostructures.

"The pNT molecules are aligned and packed in a lattice rich with pores and voids," he adds. "These nanopores can encapsulate various substances which imbue the pNT crystal with properties useful in electronic applications."

As an example, the researchers embedded fullerene C_{70} molecules into the pNT pores (Fig. 2). The porous nature of the new molecule could form the basis of novel composite materials, which might be of particular interest as high capacity electrode materials for solid-state lithium ion batteries.

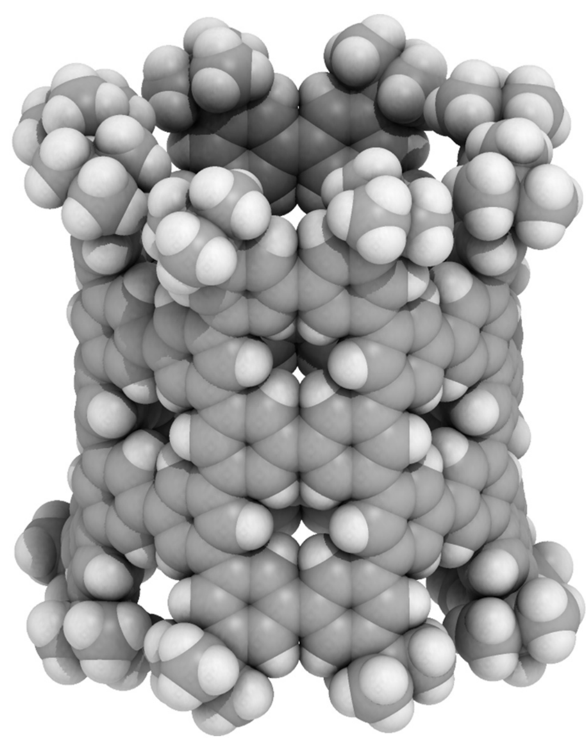

Fig. 1. Nanometer-sized pNT cylinder made of 40 benzene units.