

Forging the Links to Building Better Metal Oxides

Metal oxides such as titanium dioxide (TiO_2) are fascinating and versatile substances that can be used in many applications, including photovoltaic devices, batteries, and other vital technologies. But the utility of a particular material for a particular purpose may be limited, and common techniques to chemically "fine tune" their properties to fit specific parameters, such as doping or surface coating, are not always practical or effective. A group of researchers from a diverse set of institutions decided to try a different strategy by cross-linking metal oxide molecules with boron to create clusters of hybrid networks with new chemical and electrical properties and then characterizing the material at the APS. Their work opens possibilities for the precise tailoring of such materials for specific purposes.

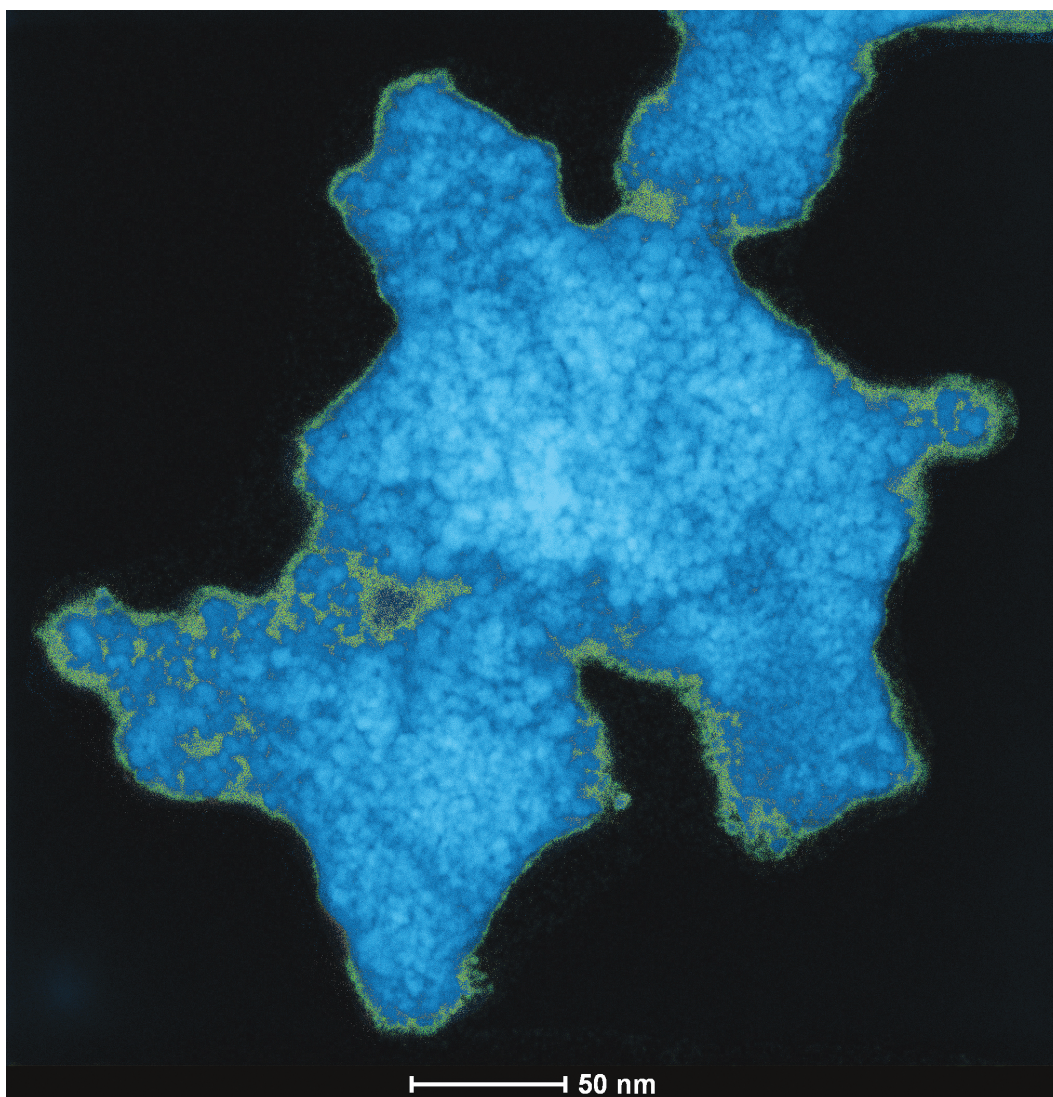


Fig. 1. A scanning transmission electron microscope image of TiO_2 nanoparticles cross-linked with boron-rich clusters.

The team's approach involved identifying a robust boron-containing cluster capable of withstanding the harsh conditions inherent in the cross-linking processes. The researchers from the University of California, Los Angeles; the University of California, Santa Barbara; Cairo University (Egypt), Purdue University; Argonne National Laboratory; and the University of Oregon settled on a three-dimensional aromatic benzene analog, $[\text{N}^i\text{Bu}_4]_2[\text{B}_{12}(\text{OH})_{12}]$, which is a derivative of dodecaborate of the $[\text{B}_{12}(\text{OH})_{12}]^{2-}$ type. After annealing a bulk sample at 500°C in air, creating a cross-linked polymer of clusters and boron oxide, the researchers combined the substance with titanium tetraisopropoxide, resulting in the formation of a shiny black solid hybrid material. They used various techniques to analyze this material's physical and electrochemical characteristics, including x-ray absorption spectroscopy at the

MR-CAT 10-BM-A,B x-ray beamline at the APS, and total scattering data suitable for pair distribution function (PDF) analysis collected at XSD beamline 11-ID-B beamline at the APS.

Structural analysis of the material utilizing a variety of methods including powder x-ray diffraction, scanning electron microscopy, transmission electron microscopy (Fig. 1), x-ray photoelectron spectroscopy, nuclear magnetic resonance imaging, and PDF showed crystalline anatase TiO_2 in densely embedded nanocrystals. B_{12} -based clusters were also present, leading to the present model of a hybrid molecular boron oxide comprised of cross-linked intact boron clusters and boron oxide, with embedded nanocrystals of anatase TiO_2 .

The experimental team next investigated the material's electronic properties. Because dodecaborate derivatives have been previously shown to exhibit pseudo-metallic redox activity, the researchers looked for clusters in redox states. Electroparamagnetic resonance spectroscopy and superconducting quantum interference device magnetometry showed that the material is paramagnetic, which appears to be related to the cross-linked molecular boron oxide material. The material also showed an electron transfer rate considerably higher than that of either anatase or rutile TiO_2 , indicating its ability to enhance electronic properties when linked to metal oxides.

To further investigate these characteristics, the experimenters constructed pouch-cell supercapacitors using the material in the active layer. These showed superior capacitance and performance compared to both TiO_2 forms, which appears to be directly related to the cross-linked molecular nature of the hybridized material. Combined with the reduced charge-transfer and ionic diffusion resistance of nanosized TiO_2 , these properties could make this material highly desirable for energy storage applications.

The study group also examined the hybrid material's potential use in visible light photochemical processes by testing it as a photocatalyst in the decomposition of various water contaminants. Under a low-power LED red-light source, three common dye contaminants showed markedly faster degradation with the new material than with a pristine TiO_2 control. Visible light excitation appears to stimulate electron transfer and generate reactive oxygen species that efficiently break down organic contaminants. The lack of precious metal elements in the new material makes it an even more attractive and inexpensive candidate for such applications.

While the current experiments provide an excellent demonstration of how the properties of common metal oxide materials can be altered and enhanced through molecular cross-linking techniques, the researchers note that further work is needed to better understand the underlying chemistry and enable more exact and controlled modifications. One possibility is to expand the technique with the use of other metal oxides such as ZrO_2 . Nevertheless, the significantly enhanced properties achieved in the material synthesized in these experiments makes this relatively simple, room-temperature approach to molecular customization enormously promising, not only for TiO_2 but also other metals and materials. — Mark Wolverton

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