Department of Physics and Astronomy
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Closing the Gap

Tuning Titanium Oxide to Let the Sun Shine In

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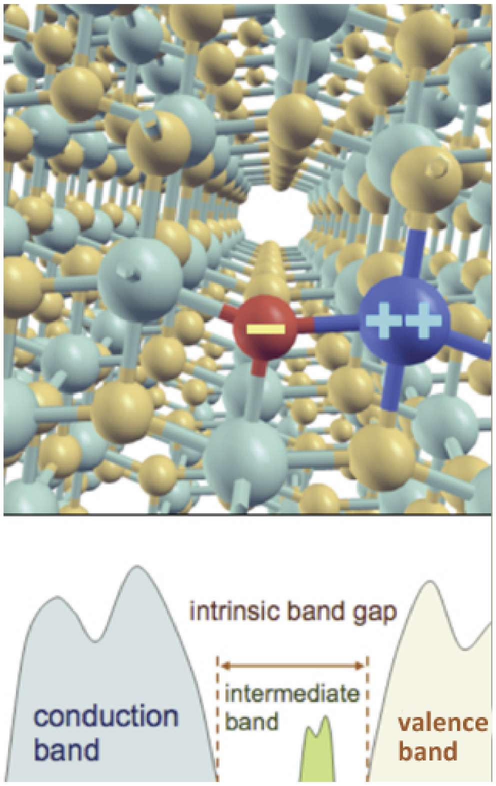
You may know titanium oxide ($Ti0_2$) from the more everyday parts it has played; an inexpensive white pigment in sunscreen or paint, for example. But with a little tuning from UTK physicists and their colleagues at Oak Ridge and Argonne National Laboratories, this material could land a starring role in the conversion of sunlight to energy for everyday life.

As a photocatalyst, titanium oxide absorbs particles of light and in the process generates charge carriers that break apart water molecules and produce hydrogen gas. It’s a robust material that can withstand harsh conditions, and so has great promise for solar energy and environmental cleanup. Yet its efficiency has been hampered by its large “band gap.”

$Ti0_2$ is a semiconductor, meaning it can act like an insulator but also like a conductor. Semiconductors host electrons in different energy bands, separated by a gap. The lower is the valence band, which is usually brimming with electrons. The upper is the conduction band, which is typically either empty or home to only a few fleeting electrons, as energy is needed to get them there from the lower, valance band. With a rise in temperature or the addition of light, however, the electrons in the valence band can absorb enough energy to cross the energy gap and hop to the conduction band, where they are free to roam around, becoming carriers. Unfortunately, the gap between the bands is so large that $Ti0_2$ can absorb only ultraviolet light; not the more abundant visible light needed for more efficient solar energy conversion. UTK Physicists Wenguang Zhu, Violeta Iancu, Hanno Weitering, and Zhenyu Zhang were part of the research team that found a way to bridge this gap.



Schematic illustration of noncompensated anion-cation codoping. Upper panel: Atomic structure of a non-compensated pair in anatase $Ti0_2$.
Lower panel: Formation of an intermediate band in the gap region via noncompensated anion-cation codoping.

A common approach for altering the properties of semiconductors is adding foreign impurities to the host material, a process called doping. In titanium oxide, this has yet to produce a breakthrough because the thermodynamic solubility of most dopants is extremely low. Working with scientists from Oak Ridge and Argonne National Laboratories, UTK’s physicists went back to basics, using first-principles calculations to come up with the best combination of dopants to be readily placed inside TiO_2 and narrow the gap between the bands. Ultimately, they chose to use positively-charged ions (cations) and negatively-charged ions (anions) of the elements chromium and nitrogen. The key relies on the proper proportion.

The UTK/ORNL/ANL team drew their idea from everyday life experience: when a stream is a bit too broad to jump over, one could throw a few stepping stones in the middle of the stream, and jump over with multiple steps.

In the case of TiO_2, when added to the semiconductor, anions will “accept” outer electrons from the material’s existing structure, leaving a “hole” in the electron’s place. Conversely, cations will donate electrons to the host. The research team decided on a “non-compensated” configuration with a single acceptor and two donor ions, meaning the electrons added and the holes left behind would not compensate one another. They found that this ensures the creation of intermediate electronic bands in the gap region. These intermediate bands serve as the “stepping stones,” effectively building a bridge between the valence and conductance bands, and consequently increasing the amount of visible light that titanium oxide can absorb. An added benefit was that these intermediate bands could be tuned by choosing different combinations of anion-cation pairs and changing the doping concentration.

The hypothesis was validated by experiments using scanning tunneling spectroscopy (STS) and electron paramagnetic resonance (EPR) spectroscopy. The STS technique uses a scanning tunneling microscope to show the position of individual atoms, while EPR reveals the properties of unpaired electrons. The findings could lead to the development of a new class of titanium-oxide-based photocatalysts for solar energy conversion, hydrogen generation from water, and a variety of industrial and environmental applications. The potential for tailoring the band gap in semiconductors may also prove instrumental in a wide range of advanced materials for catalysis, optoelectronics, spintronics, and clean energy.

The work is described in the paper “Band Gap Narrowing of Titanium Oxide Semiconductors by Noncompensated Anion-Cation Codoping for Enhanced Visible-Light Photoactivity,” published in *Physical Review Letters* in late November. It earned the “Editor’s Suggestion” distinction as one of a group of papers the journal’s editors highlight each week to promote reading across fields, and was also featured in the “breakthroughs in technology” section of *Forbes* magazine.

Zhu, the lead author, is a research assistant professor in the physics department. Iancu was a post-doc with Weitering’s research group, having recently accepted a new position with the Katholieke Universiteit in Leuven, Belgium. Both Weitering and Zhang hold joint faculty professorships with appointments in the UTK Physics Department and ORNL’s Materials Science and Technology Division. Their collaborative team also comprised Xing-Qiu Chen, Gyula Eres, Baohua Gu, Harry M. Meyer, III; Hui Pan, M. Parans Paranthaman, Xiaofeng Qiu, G.M. Stocks and Wei Wang, all of ORNL; and Nada M. Dimitrijevic and Tijana Rajh of Argonne National Laboratory.