

Being unable to work in a laboratory, this summer's research attended to the foundational literature and concepts in the field of metal oxide photocatalysts – one where undergraduate exposure is often lacking. Each week focused on a specific unpinning of metal oxide photocatalysts, which culminated in a series of self-contained educational presentations designed for chemistry undergraduates. Selected topics are presented here, each building on the last for those without much, if any, chemistry background.

Semiconductors and the PN Junction

Conductors are materials which freely conduct electricity due to their loosely held electrons. Large metal atoms have a weak hold on their outermost, or *valence*, electrons and fit nicely into an ordered structure called a *lattice*, both of which contribute to their conductivity. Small-atom materials lacking free electrons, like plastic polymers, are called *insulators*, and do not conduct electricity.

This binary definition of conductors and insulators falls apart examining the elements of Group 14 (e.g. Si, Ge, etc.) which contain 4 electrons in their valence shell. The bonds between Group 14 are *covalent*, with each atom sharing half of the number of electrons needed to form four bonds (See Figure 1). If one of the atoms in this lattice gains sufficient thermal energy, it may break an existing bond, creating a free electron (as well as a free, positive *hole*, which helps us model charge in molecules) and allowing current to flow. This conditional conductivity is what earns a *semiconductor* its name. To improve the conductance of a semiconductor, we can *dope* it with a Group 13 or Group 15 atom. The effect of this is illustrated in Figure 1; in both cases, an extra electron or hole is present from the beginning, so the material can conduct slightly even before the high energy bond breakage. Depending on the charge carrier, the semiconductor is either *N-* (electrons) or *P-* (holes) *type*.

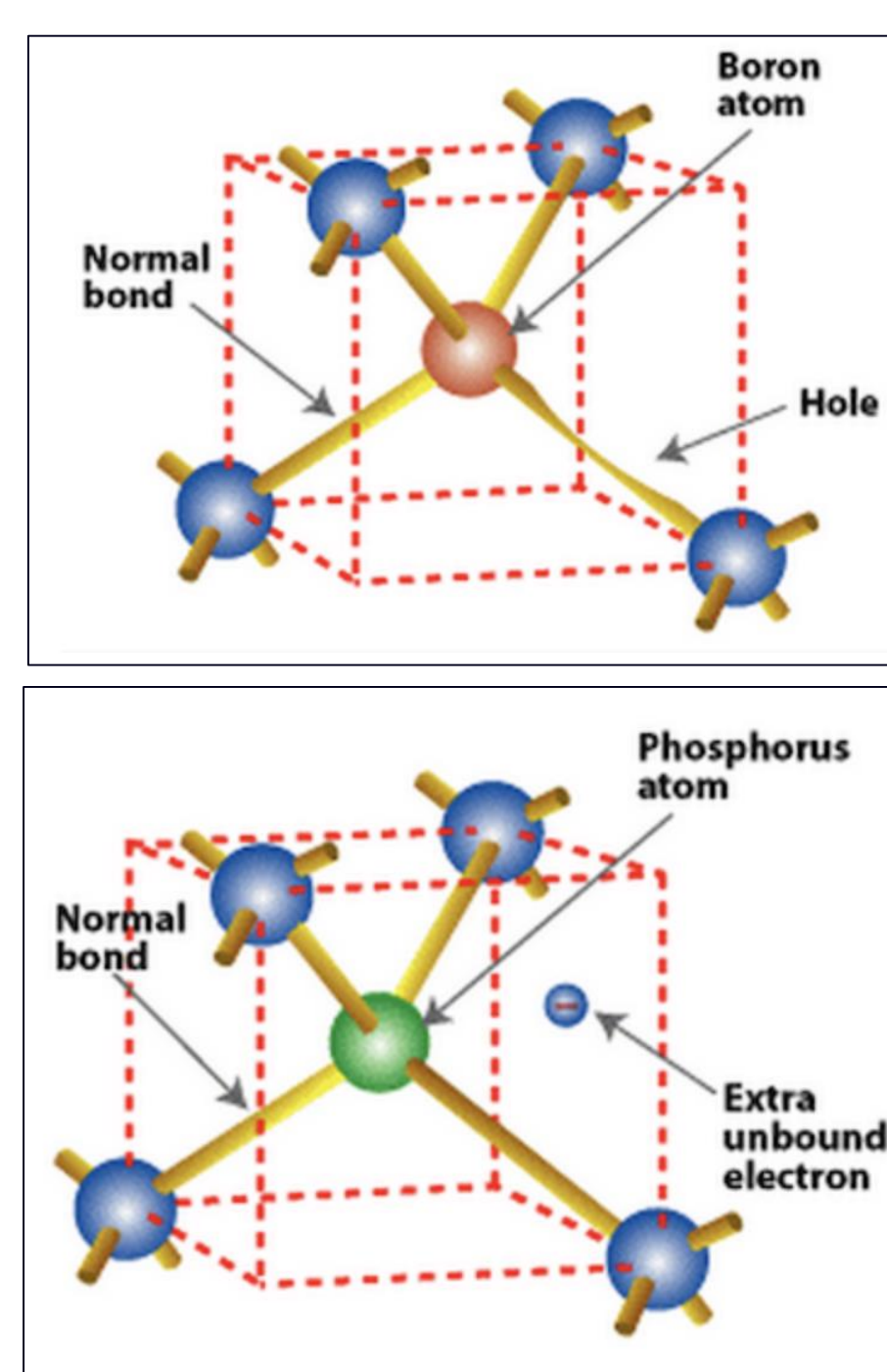


Figure 1: Top: a P type semiconductor. Bottom: an N-type semiconductor. Source: Candler, K., et al.

When an N and P-type semiconductor meet, they form a *PN-junction*, which has interesting electronic properties. The difference in the concentration of electrons between the N and P-type semiconductor causes a electrons to move to toward the “emptier” P-type side. This migration causes the P side to have a negative charge, which establishes an *electric field* from the positive N to the P side. These two effects oppose each other to create a region devoid of charge carriers, called a *depletion zone*. An external potential (*voltage*) would be required to push electrons and holes towards the depletion zone, thinning it and allowing current to flow once again.

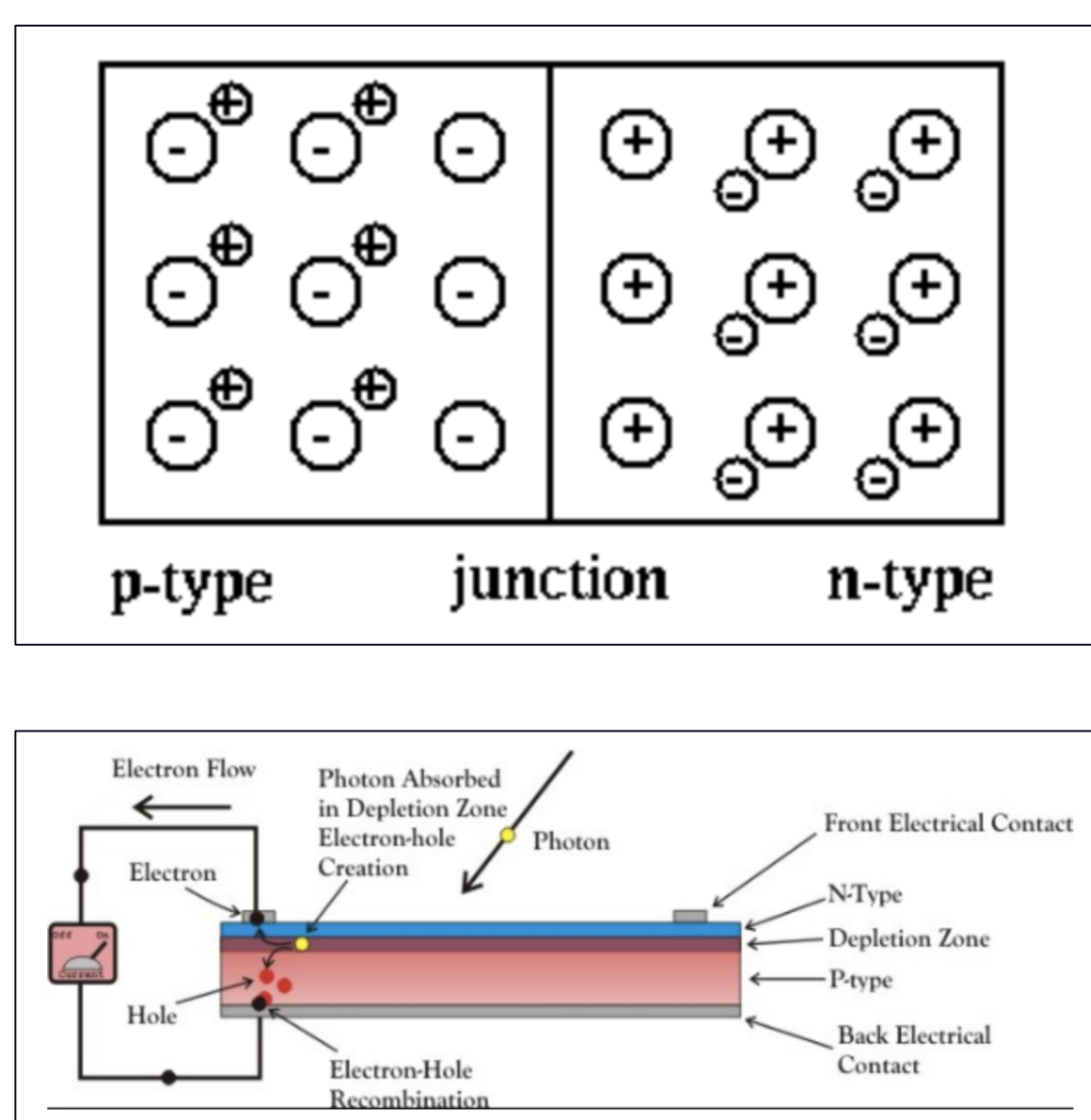


Figure 2: Top: a PN junction. Bottom: a cross section of a solar cell, revealing a PN-junction at work. Source: Candler, K., et al.

Band Theory and Band Bending

Electrons in a molecule can only occupy certain discrete energy levels called *molecular orbitals*. Although this is effective for modelling smaller atoms, it becomes unruly for larger molecules. The abundance of occupiable states creates orbitals which begin to blend, better modelled by two continuous bands of occupiable states. The lower energy band, where electrons reside in the *ground*, or unexcited, state is called the *valence band*, while the next highest state these electrons could occupy forms the bottom of the *conductance band*. The size of unoccupiable region of space between them, called the *band gap*, determines the energy needed to excite an electron.

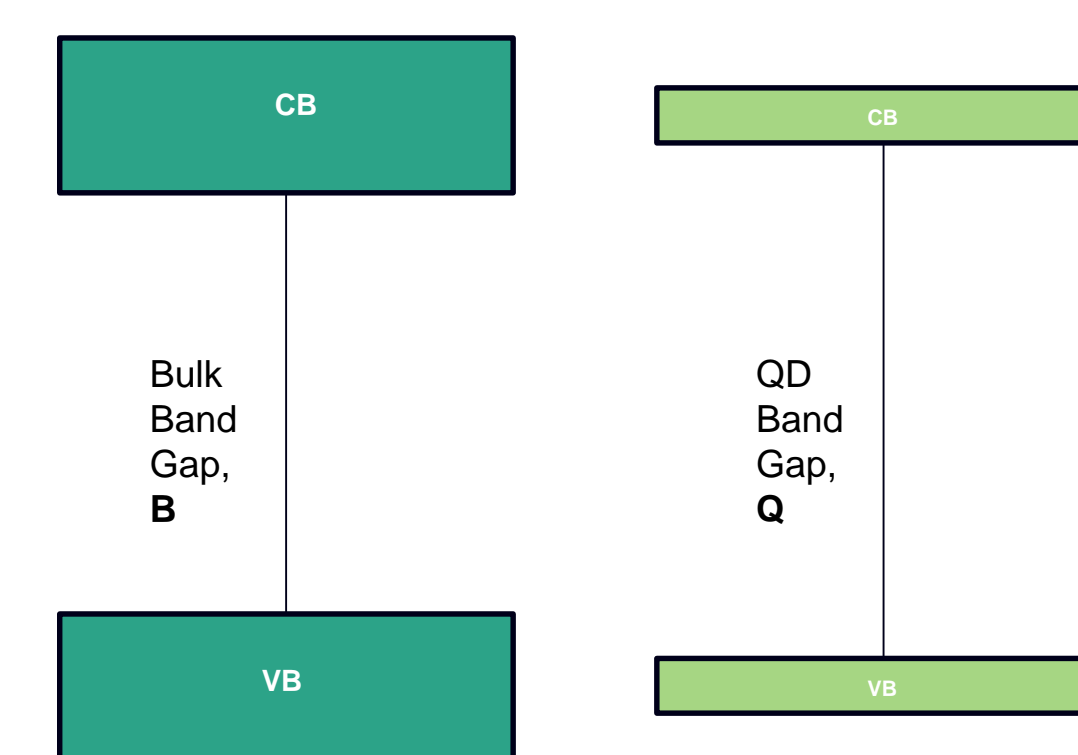


Figure 3: As fewer atoms overlap to create the aggregate band, the band width gets narrower. The overall bandgap is greater for the smaller material, or $Q > B$.

Band theory is valuable for examining the electronics of *heterojunctions*, interfaces between different materials. When two materials meet, their valence and conductance bands will bend upwards or downwards to create an interface with unique electronic properties (e.g. PN-junction). Band theory also explains the importance of size in semiconducting materials. Bands in a *bulk* material, or non-nanomaterial, are comprised of many orbitals, but as atoms are removed, the number of available states in both bands is reduced. This reduces the width of these bands, and the size and energy of the band gap increases as a result (See Figure 3). Thus, a very small particle will have a much greater band gap than that associated with the bulk material (See Future Studies section).

Quantum Dots and Quantum Confinement

A *quantum dot* (QD) is a *nanocrystalline* (2-10 nm, or 1-50 atoms) semiconductor whose electronic and optical properties are size-dependent. QDs fall in a unique size range which allows them to be treated like a single atom while also being well-modelled by band theory. The difference between a QD and an atom comes from how charges are thought about. In essence, a QD has a particle called an *exciton*, which is a combination of an excited electron in the conductance band and a positive hole in the valence band. It is often called an exciton pair due its combinatory nature.

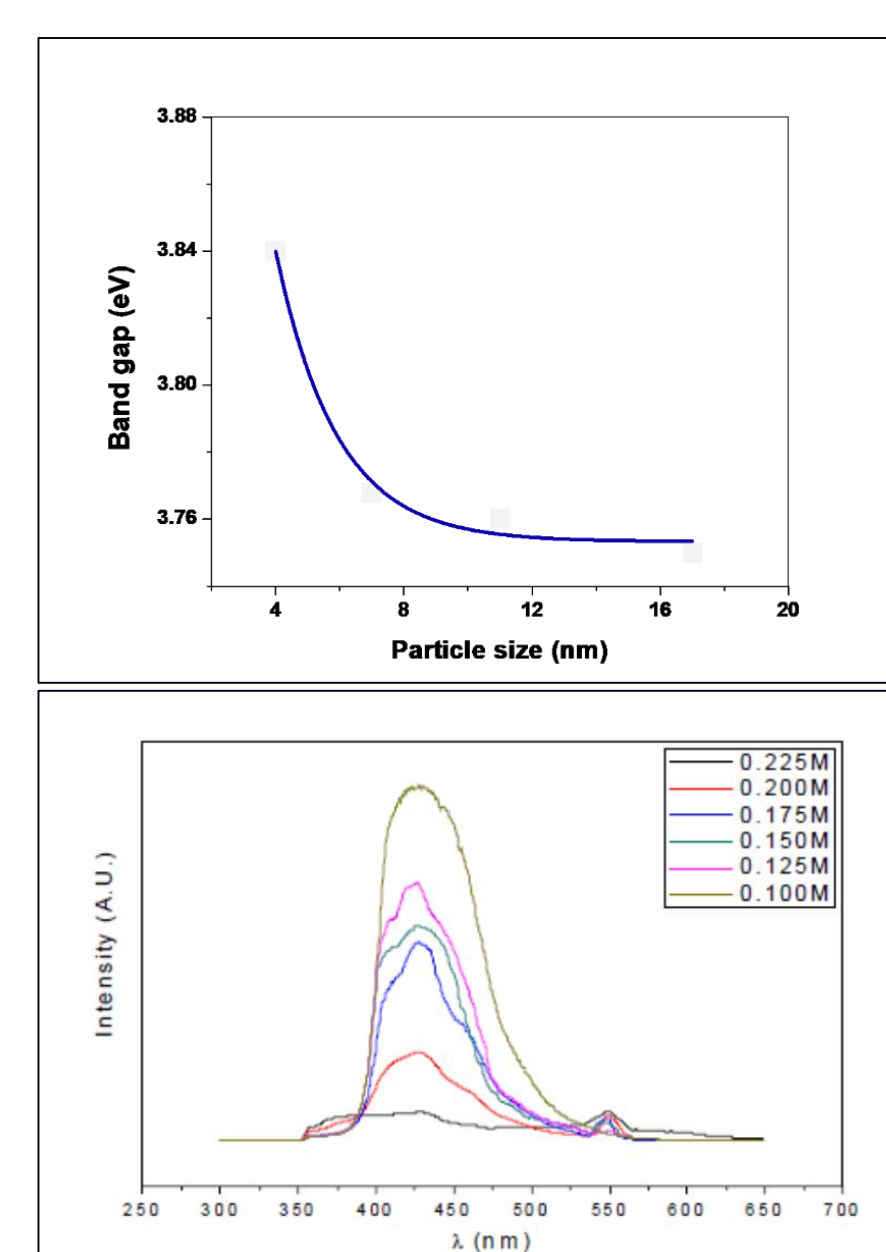


Figure 4: Top: band gap of ZnO based on particle size. Bottom: Photoluminescence of ZnO based on size. Source: Samanta, P.K., et al.

A QD, by definition, is subject to *quantum confinement*, an increase in internal energy from the forced proximity of exciton pairs. Band theory describes the increase in band gap (and decrease in each band's width) associated with the shrinkage of a bulk material (See Band Theory section). The exciton pairs are forced into close proximity of one another because of the decrease in band width, and the repulsions between excitons increase the energy of the QD. The energy associated with quantum confinement plus the energy of the band gap define the total internal energy of the QD, which creates a complete picture of the electronic environment of the material.

Wulff Constructions

The characterization of a nanomaterial is incomplete without considering the structure and shape. Luckily, all nanocrystalline materials will have an *equilibrium crystal shape*, which minimizes the intrinsic energy associated with surface of the particle. However, the packing of atoms into a crystal lattice is *directional* and dependent on the orientation, which means there is no single universally preferred crystal structure.

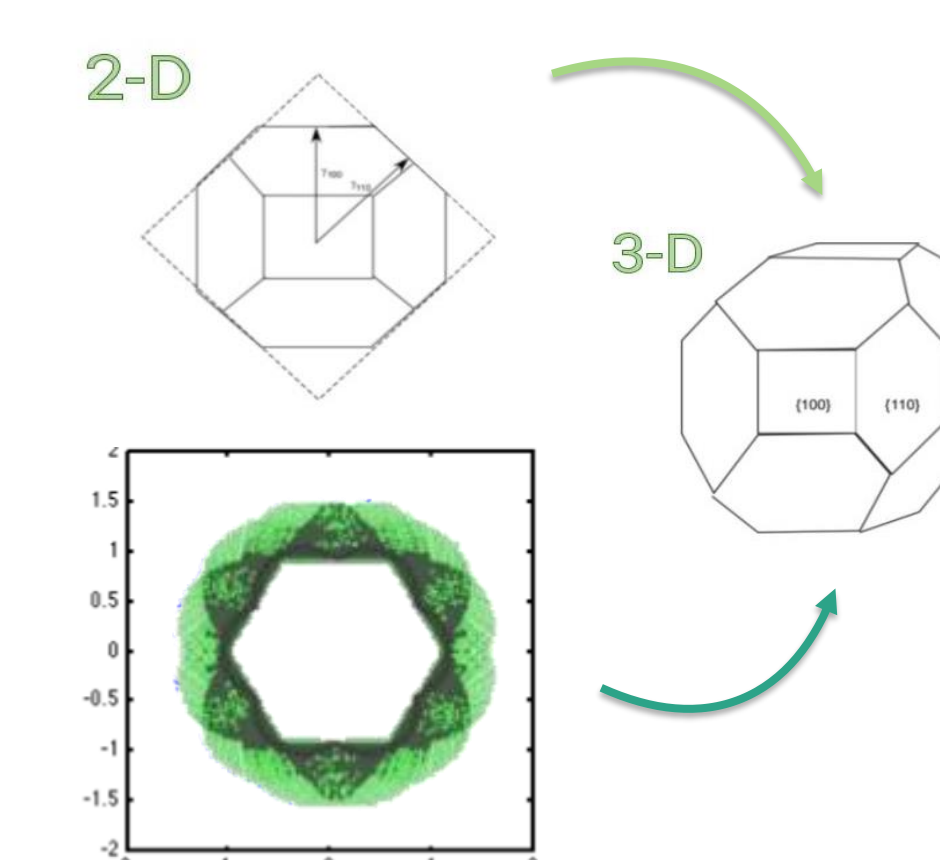


Figure 5: The Wulff Construction is constructed in 2-D by software or by hand, and then extrapolated into 3-D to reveal the shape of the molecule.

The *Wulff theorem* lets chemists predict the particle shapes. Its main postulate is that surface energy is minimized when the distances of each face to the center point of the lattice are proportional to the surface energy of that face. Mathematically, the surface energies can be represented by *vectors*, which can be plotted on a special coordinate system called a *polar plot*. A series of lines drawn perpendicular to these vectors at their ends creates the shape (See Figure 5). This simple way of determining crystal shape reveals the location of the highest-energy faces where chemical reactions occur.

Nanoparticle Synthesis

There are hundreds of ways to make nanoparticles, but the most promising are *chemical methods*, which use molecular *precursors* to create atomically precise nanoparticles (<10 nm). Most of these chemical methods are classified as *solution-phase* processes, consisting of two regimes: the *nucleation regime*, where the first and smallest molecules (*nuclei*) are formed, and the *growth regime*, where nuclei combine and grow. Chemists focus on separating these two regimes to the greatest possible extent to achieve uniformly sized particles.

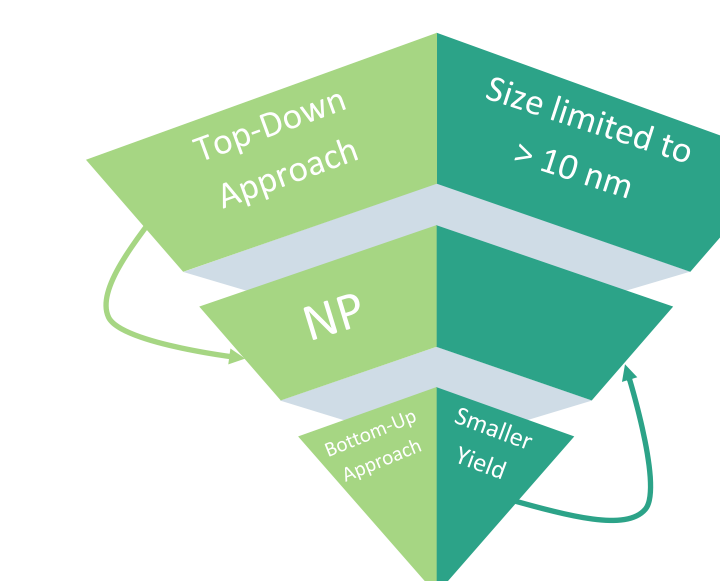


Figure 6: Top-Down vs. Bottom-Up synthesis strategies

Future Studies

With labs reopening, this accumulated knowledge can finally be applied to a nanoparticle of interest: TiO_2 . Recently, I was able to perform a solution-phase synthesis of a nano-catalyst and perform some rudimentary data analysis. Figure 7, shows the *ultraviolet-visible light spectra* of the synthesized particle. A tangent line has been approximated to the maximum of the first derivative (the black dotted line), and where it intersects the x-axis is the band gap of the particle! Here, the calculations revealed that the particles synthesized were around 2 nm, a valid quantum dot. The concepts presented here appear in virtually every real application of metal oxide photocatalysts, opening up exciting new avenues of research for budding materials chemists.

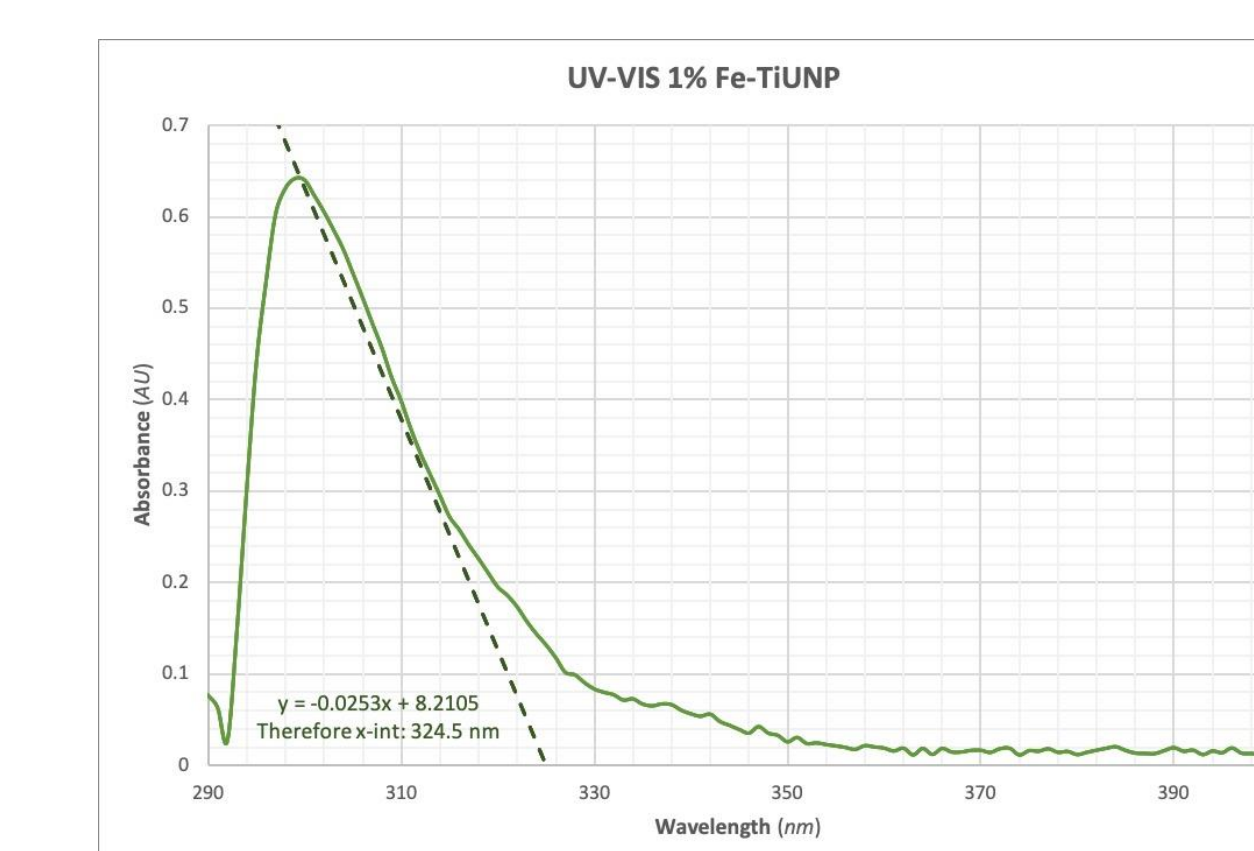


Figure 6: Ultraviolet-Visible Light spectra of Iron-doped TiO_2 at a 1% by atom doping level