Tetrahedrally-Coordinated, TiO$_2$-Based Nanocomposites for Solar Fuel Production

Michael Campos, Gray Research Group

![Diagram of nanocomposites](image)

Figure 1. The three classes of nanocomposites investigated. a) Isolated TiO$_2$ on SiO$_2$. b) TiO$_2$ ALD on SiO$_2$ plus an organic precursor, later removed (“nanobowls”). c) TiO$_2$-core, Al$_2$O$_3$-shell decorated with isolated TiO$_2$

Recent findings in the Gray Group have suggested the importance of under-coordinated titania as an active site in CO$_2$ photoreduction. It is not clear exactly what role these active sites play in photocatalysis, however. Do these sites trap charges and facilitate electron transfer to adsorbed CO$_2$? Do they serve as binding sites for CO$_2$? Do they do both? Due to the known templating effects of tetrahedrally-coordinated silica, several formulations of titania-silica nanocomposites were synthesized and investigated. Additionally, several previously established silica-titania photocatalysts prepared by sol-gel methods were synthesized and subjected to the same tests as the novel materials featured in this project. Can the high photoactivity of these materials be explained by the presence of undercoordinated titania? Are there benefits to controlled synthesis of active sites?

The first class of nanocomposites (Figure 1a) was prepared by treatment of silica spheres with organotitanium precursors of various levels of bulkiness, followed by calcination. The second class of materials (Figure 1b) was prepared by grafting an organotitanium mask on the SiO$_2$ surface followed by several cycles of TiO$_2$ atomic layer deposition (ALD) before removal of the organic by calcinations. This allowed for the formation of a thin light-absorbing TiO$_2$ layer and “nanobowls” that expose the silica-titania interface. The third class of materials (Figure 1c) was prepared by Al$_2$O$_3$ ALD onto a titania core, followed by decoration with isolated titania sites, as in the first class. This inert Al$_2$O$_3$ layer allowed for the separation of light harvesting by bulk titania and surface reactivity by under-coordinated titania. Sol-gel materials were prepared via simultaneous hydrolysis of organotitanium and organosilicon precursors, followed by calcination.
To screen the materials for photoactivity, their catalytic activities were measured in photo-oxidations of benzyl alcohol (5 mM) to benzaldehyde, an established protocol in our laboratory which uses equal catalyst masses. A 365 nm Pen-Ray lamp was used as a light source, and products were observed by gas chromatography. Type 1a materials exhibited little light-absorbing capacity (band gap of 3.4-3.8 eV), corresponding to relatively small amounts of titania in the nanocomposites. The 1b materials, on the other hand, were able to absorb light more effectively, with band gaps near ~3.3 eV. Representative results from selected formulations of material 1b are shown in Figure 2. As shown, 1b materials—silica spheres coated with several layers of titania, with built-in “nanobowls”—far outstripped the corresponding materials without the organic precursor.

The photo-oxidation results of type 1c materials are shown in Figure 3. From preliminary results, there appears to be a direct correlation between the incidence of under-coordinated titania and benzaldehyde production, suggesting not only under-coordinated titania as the active site, but also that charges can be passed through inert oxide layers effectively enough to carry out such catalysis. From these exciting results one can envision an entire class of photocatalysts that decouple the phenomena of light absorption and surface functionality.

The sol-gel materials exhibited light-absorbing capacities similar to bulk titania, with band gaps in the range of 3.2-3.3 eV; however, as seen in Figure 4, a sharp drop-off in reactivity was observed between Ti:Si ratios of 55:45 and 60:40. This may be attributable to a smaller catalytic surface area due to crowding by silica, or it might simply correlate with less titania present in the composite. The most photoactive sol-gel materials were shown to be somewhat more active than the novel nanocomposites thus far, but this is pending analysis by catalyst surface area as well as the improvement of nanocomposite design.

Moving forward, the next step will be to test promising photocatalysts in CO₂ photoreduction. It was not possible to carry this out in the past months because of an irreparable leak in the gas-phase photoreactor. Other avenues to pursue include characterization of active sites by EPR and XANES, as well as probing the limits of how thick a shell can be in a functional core-shell material—i.e. how far electrons can be passed through an inert oxide layer.