Visible-Light Photochemical Activity of Heterostructured Core–Shell Materials Composed of Selected Ternary Titanates and Ferrites Coated by TiO₂

Li Li,† Xuan Liu,† Yiling Zhang,† Noel T. Nuhfer,† Katayun Barmak,‡ Paul A. Salvador,† and Gregory S. Rohrer*†

†Department of Materials Science and Engineering, Carnegie Mellon University, Pittsburgh, Pennsylvania 15213, United States
‡Department of Applied Physics and Applied Mathematics, Columbia University, New York, New York 10027, United States

ABSTRACT: Heterostructured photocatalysts comprised of microcrystalline (mc-) cores and nanostructured (ns-) shells were prepared by the sol–gel method. The ability of titania-coated ATiO₃ (A = Fe, Pb) and AFeO₃ (A = Bi, La, Y) catalysts to degrade methylene blue in visible light (λ > 420 nm) was compared. The catalysts with the titane cores had enhanced photocatalytic activities for methylene blue degradation compared to their components alone, whereas the catalysts with ferrite cores did not. The temperature at which the ns-titania shell is crystallized influences the photocatalytic dye degradation. mc-FeTiO₃/ns-TiO₂ annealed at 500 °C shows the highest reaction rate. Fe-doped TiO₂, which absorbs visible light, did not show enhanced photocatalytic activity for methylene blue degradation. This result indicates that iron contamination is not a decisive factor in the reduced reactivity of the titania coated ferrite catalysts. The higher reactivity of materials with the titane cores suggests that photogenerated charge carriers are more easily transported across the titanate–titanate interface than the ferrite–titanate interface and this provides guidance for materials selection in composite catalyst design.

KEYWORDS: core–shell, photocatalyst, TiO₂, dye degradation, ferrite, titanate

1. INTRODUCTION

TiO₂ is one of the most widely studied photocatalysts because of its appropriate electronic structure, photostability, chemical inertness, and commercial availability.¹–⁷ Titania’s photochemical efficiency in visible light is limited by several factors, such as the recombination of photogenerated charge carriers, the back reaction of intermediates, insufficient active sites for the redox reactions, and especially its wide band gap. Various methods have been used to modify TiO₂ to make it more active under visible light, such as metal and nonmetal doping,³⁻¹² dye sensitization,¹³,¹⁴ the formation of junctions with other semiconductors¹⁵,¹⁶ and coupling to narrow band gap semiconductors.¹⁷–²⁴ For example, CdS,²⁵ Cu₂O,²⁶ BiOCl,²² ZnFe₂O₄,²⁷ and CuInS₂²⁸ were combined with TiO₂ for visible-light sensitization and the heterostructured materials showed enhanced reactivity for organic pollutant degradation and hydrogen production.

The combination of titania with different semiconductors is potentially promising because heterostructured photocatalysts can combine multiple functionalities within a single structure.²⁴,²⁹ Among different configurations for heterostructured photocatalysts, the core/shell structure has been widely investigated as a means to enhance light absorption, charge transfer, and surface area.³⁰,³¹ Several heterostructured catalysts comprised of micocrystalline, visible light absorbing cores (FeTiO₃ and PbTiO₃), coated by nanostructured titania, have recently been shown to have enhanced visible light photochemical reactivity.³²,³³ These materials combine the high surface area that is necessary to provide enough active sites for high reactivity with the good crystallinity required to transport photogenerated carriers without recombination.³⁴ Finally, the addition of an internal field within the light absorbing core separates photogenerated charge carriers and thus decreases recombination. This internal field can arise from different sources, such as ferroelectric spontaneous polarization,³⁵–³⁷ or polar surface terminations.³⁸,³⁹ For example, a BaTiO₃/TiO₂ core/shell heterstructure shows enhanced photocatalytic hydrogen production compared to its components alone.⁴⁰

On the basis of the success of FeTiO₃/TiO₂, PbTiO₃/TiO₂, and BaTiO₃/TiO₂ heterstructured catalysts with micocrystalline cores and nanocrystalline shells, it is reasonable to hypothesize that cores with narrower gaps will absorb more visible light and be more reactive. The purpose of this paper is to test this hypothesis. In general, ferrites have narrower bandgaps than titanates, so we will compare the photochemical activities of heterostructured catalysts with Fe containing cores

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to those with Ti containing cores. Specifically, ABO₃ cores with Fe on the B site (BiFeO₃, LaFeO₃, YFeO₃) and with Ti on the B site (FeTiO₃, PtTiO₃) were coated by TiO₂ and their abilities to degrade methylene blue were compared. In each compound, the B cation is octahedrally coordinated by oxygen. Note also the Fe in FeTiO₃ is divalent and is on the A-site, so it is considered a titanate; in the ferrites, the Bi, Y, and La cations are on the A-site and are trivalent. All of the compounds have perovskite-related structures, except FeTiO₃ which has the illmenite structure. This collection of core materials includes some that are ferroelectric (PtTiO₃, BiFeO₃) and some that are not (LaFeO₃, YFeO₃, FeTiO₃), as well n-type and p-type materials. In all the heterostructures, the cores selectively absorb the light used to promote the reaction, which is too low in energy to promote excitation in the titania shell. The enhanced reactivity of the composites with titanate cores compared to the ferrite cores suggests that the transfer of charge from the core to the shell is less efficient in the ferrite/titanate heterostructures.

2. EXPERIMENTAL SECTION

Core Materials Preparation. PbTiO₃ (99.9%, Alfa Aesar) and FeTiO₃ (99.8%, Alfa Aesar) microcrystals or powders were obtained from commercial sources. (Bi, La, Y)FeO₃ microcrystals were produced using methods described below. BiFeO₃ was prepared using a modification of a previously reported hydrothermal method. Equal amounts of 0.005 mol bismuth nitrate pentahydrate (Bi(NO₃)₃·5H₂O, Acros Organics, 98%) and iron nitrate nonahydrate (Fe(NO₃)₃·9H₂O, Acros Organics, 99%) were used as the starting materials and dissolved into 50 mL of a 0.5 M dilute nitric acid (HNO₃, Acros Organics, 68%) solution with magnetic stirring at 70 °C for 30 min. After complete dissolution, a 9 M potassium hydroxide (KOH, Acros Organics, 85.3%) solution was added dropwise into the solution above with constant stirring to coprecipitate Bi(OH)₃ and Fe(OH)₃. The pH of the final solution was adjusted to be 14. The resulting brown precipitate was filtered and washed several times using distilled water to remove K⁺, OH⁻, and NO₃⁻ ions. Next, 50 mL of KOH was mixed with the precipitate in a 100 mL beaker. Potassium nitrate (KNO₃, Acros Organics, 99.4%) was added into the mixture as a comineraler to control the growth of the powders. The suspension was stirred and dispersed at room temperature for 20 min and then transferred to a 125 mL acid digestion vessel with Teflon PFA inner walls (Parr Instrument Company). The vessel was kept at 180 °C for different durations under auto generated pressures (related to the temperature and amount of water). After natural cooling to room temperature, the products were collected and washed with distilled water by centrifugation for several times to remove the residual K⁺, OH⁻, and NO₃⁻ ions. Finally, the product was dried at 80 °C for 5 h.

LaFeO₃ microcrystals were produced using the EDTA-initiated sol–gel method. 1.4 mol of EDTA (C₁₀H₄N₉O₈, Acros Organics, 99%) per mole of metal was dissolved into water at ambient temperature. 45 mL ammonia (NH₄OH, Fisher Scientific, 29.04%) was added dropwise, as slowly as possible, into the EDTA solution to keep the pH around 7. 0.03 mol lanthanum nitrate hexahydrate (La(NO₃)₃·6H₂O, Acros Organics, 99.99%) and iron nitrate nonahydrate were mixed with the EDTA/ammonia solution. During this process, precipitation was avoided. The mixture was heated at 60 °C for 3 h and then transferred to a drying oven for 2 days to form the black gel. The gel was then ground into powder and calcined at 600 °C (at a heating rate of 10 °C/min) for 24 h to burn off the organic component. The calcined powder was then annealed at 900 °C for 24 h (heated at 10 °C/min) for crystallization. The final product was collected after grinding the calcined powder. YFeO₃ was synthesized using a method similar to that used for LaFeO₃. YFeO₃ was fabricated using a sol–gel method with citric acid as a linking reagent. 0.03 mol yttrium nitrate hexahydrate (Y(NO₃)₃·6H₂O, Acros Organics, 99%) and iron nitrate nonahydrate (Fe(NO₃)₃·9H₂O, Acros Organics, 99%) were dissolved into 100 mL of a 0.72 mol/L citric acid (C₆H₅O₇, Acros Organics, 99.5%) solution; 26.3 mL ammonia was then slowly added to the mixture. The pH of the solution was neutral and stirred for 3 h at 60 °C. The solution was then dried at 130 °C for 2 days to form a xerogel. The xerogel was then calcined and sintered in exactly the same way as the LaFeO₃.

AFO/TiO₂ Heterostructure Preparation. AFO, microcrystals were coated with TiO₂ using the sol–gel method by the hydrolysis of TBT (Ti(OC₄H₉)₄, Acros Organics, 99.0%). The AFO microcrystals were suspended in 29 mL of ethanol/water (20 mL/9 mL) solution and sonicated for 30 min. Ten milliliters of acetic acid was added to adjust the pH. Another solution was prepared with a suitable amount (15 mL) of ethanol, 8.6 mL of TBT, and 1 mL of 2,4-pentanedione. The transparent TBT solution was added dropwise to the AFO suspension with stirring for 2 h. The mixture was then aged at 90 °C in a water bath for 24 h. The xerogel collected from the mixture was ground and then calcined at 500 °C for 2 h with 5 °C/min heating rate to obtain the final product. FeTiO₃/TiO₂ heterostructures were sintered at temperatures between 400 and 600 °C to investigate the influence of annealing temperature.

TiO₂ nanoparticles were obtained from the same procedure, but without the addition of the ABO₃ core materials. Several control samples were also prepared. Fe-doped TiO₂ was produced by adding 1 mol % Fe(NO₃)₃·9H₂O into the precursor and otherwise adhering to the TiO₂ preparation described above. Physical mixtures of FeTiO₃ and TiO₂ were made by combining them with the mass ratio of 1:2 in ethanol and sonicating them at 80 °C for 3 h. The mixtures were then dried at 70 °C for 12 h.

Characterization. The phase composition was investigated by X-ray diffraction (XRD) using a diffractometer (PANalytical, XPert Pro, Philips) equipped with a CuKα, radiation source and operated at 45 kV and 40 mA. Diffraction patterns were collected from 10° to 90° at a scanning rate of 3°/min and a step size of 0.05° for all 2θ-2θ scans. Transmission electron microscopy (TEM, Tecnai F20), with an accelerating voltage of 200 kV, was used to characterize the morphology of the heterostructured photocatalyst. The TEM sample was prepared by dispersing the powder ultrasonically in methanol for 10 min and then distributing several drops of the suspension into a 200 mesh copper grid coated with a carbon support film. The reflectance spectra of the samples were recorded by a UV–vis spectrometer (Ocean Optics USB2000) equipped with a R600–7 reflection probe optimized for the 250–800 nm region. The Brunauer–Emmett–Teller (BET) surface area was measured by nitrogen adsorption/desorption isothermal measurement (Nova 2200e, Quantachrome, FL) at 77 K. The sample was vacuum-degassed for 3 h at 300 °C to reduce the moisture before measurement.

Methylene Blue Degradation. Methylene blue (MB) photocatalytic degradation was used to evaluate the photocatalytic properties of the powders. The dye degradation experiment was performed at room temperature in a 100 mL quartz photochemical reactor. An aqueous suspension of 0.3 g photocatalyst was added into 65 mL of 1 × 10⁻¹ M MB solution. Prior to irradiation, the suspension was stirred in the dark for 2 h to achieve absorption/desorption equilibrium between the photocatalyst and the dye. The photocatalytic reaction was initiated by irradiating the reaction system with a 300 W high-pressure mercury lamp for 5 h. A UV cutoff filter (Oriel, λ > 420 nm) with 20 cm² window was placed between the quartz reactor and the lamp to cut off the UV light. Five milliliters of dye solution was taken each hour and then centrifuged to remove the particulate photocatalyst before measuring the UV–vis absorption spectrum. The initial absorbance intensity of the solution at 663.89 nm (the characteristic absorption peak of methylene blue) was denoted as C₀. The ratio between the absorbance intensity of the sample after photocatalytic reaction and C₀ is used to evaluate the degradation of methylene blue.

3. RESULTS

XRD patterns of mc-FeTiO₃/ns-TiO₂ heterostructures and their components are shown in Figure 1a. All diffraction peaks from the heterostructures and the corresponding component
comparison with the potentially Fe-doped titania coatings, we prepared unsupported 1 mol % Fe-doped TiO$_2$. The TiO$_2$ phase in the doped TiO$_2$ powder was also anatase. The (101) and (200) diffraction peaks, respectively at 25.28° and 48.05°, were used to calculate the $a$ and $c$ lattice parameters of tetragonal anatase, as well as the unit-cell volumes. Table 1 presents the comparison of lattice parameters for undoped TiO$_2$, Fe-doped TiO$_2$ and TiO$_2$ in the mc-FeTiO$_3$/ns-TiO$_2$ heterostructure. The Fe-doped TiO$_2$ had no difference in the $a$ lattice parameter, but the $c$ parameter decreased as did the unit-cell volume. This indicates the addition of Fe$^{3+}$ leads to the shrinkage of the unit cell along the $c$ axis. Considering that the ionic radius of Fe$^{3+}$ (0.64 Å) is a little smaller than Ti$^{4+}$ (0.68 Å), it is reasonable that Ti$^{4+}$ can be substituted by Fe$^{3+}$ at low concentrations causing only a small decrease in the unit-cell volume. The lattice parameters and unit cell volume of TiO$_2$ in FeTiO$_3$/TiO$_2$ heterostructures is similar to that of undoped TiO$_2$. This indicates little Fe diffuses from the FeTiO$_3$ core to the TiO$_2$ shell.

The core–shell microstructure and morphology of mc-BiFeO$_3$/ns-TiO$_2$ heterostructured powders annealed at 500 °C was analyzed in detail using TEM. A low-magnification TEM bright-field image that includes an entire particle is shown in Figure 2a. The dark region is assumed to be the BiFeO$_3$ microcrystalline core, surrounded by a semitransparent layer.

<table>
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<th>$d_{101}(\text{Å})$</th>
<th>$d_{200}(\text{Å})$</th>
<th>$a$ (Å)</th>
<th>$c$ (Å)</th>
<th>$V$ (Å$^3$)</th>
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<td>133.0</td>
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<td>1.889</td>
<td>3.778</td>
<td>9.167</td>
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<td>3.786</td>
<td>9.308</td>
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Figure 1. X-ray diffraction pattern of (a) mc-FeTiO$_3$/ns-TiO$_2$ core/shell heterostructures, annealed at different temperatures from 400 to 600 °C, and their components; (b) mc-ferrites/ns-TiO$_2$ and mc-titanates/ns-TiO$_2$ annealed at 500 °C. The diffraction pattern of 1 mol % Fe doped TiO$_2$ is also shown. The number after the heterostructure represents annealing temperature in the preparation of the heterostructure (e.g., −400 indicates annealing at 400 °C). The peak relating to TiO$_2$ was also marked with “T” in the uppermost diffraction pattern in b.

Figure 2. TEM images of mc-BiFeO$_3$/ns-TiO$_2$ heterostructured powders annealed at 500 °C. (a) Low-magnification bright-field images of an entire particle, (b) high-magnification bright-field image of detail around the BiFeO$_3$ and TiO$_2$ interface, (c) SAED of TiO$_2$ coating, (d) HRTEM image of TiO$_2$ coating.
that is assumed to be the nanostructured TiO₂ shell. A higher-magnification bright-field TEM image, taken from the semi-transparent region, is shown in Figure 2b. In this figure, the transparent layer is clearly composed of TiO₂ nanoparticles with approximate diameters of 10–15 nm. This is consistent with the 9 nm particle diameter value calculated using the measured width of the TiO₂ XRD peak and the Scherrer equation. A sharp and clear interface can be observed between mc-BiFeO₃ core and ns-TiO₂ shell. The observations of BiFeO₃/TiO₂ are characteristic of the other core–shell materials and examples can be found in earlier publications.⁴³,³²,³³,⁴⁰

The selected area electron diffraction pattern (SAED) of the TiO₂ nanostructured coating is shown in Figure 2c. The SAED result is a ring pattern, rather than bright sharp dots, because of the polycrystalline nature of the nanostructured TiO₂ coatings. Those diffraction circles were indexed and identified as the planes of tetragonal anatase TiO₂. Figure 2d is the high-resolution TEM (HRTEM) image of TiO₂ coating. The atomic arrangement is highlighted with the white solid line. The distance between two contiguous atomic planes is measured to be 3.5 Å, which is consistent with the value of interplanar distance of the (101) planes in anatase TiO₂. These results are consistent with earlier results on heterostructured catalysts with titane cores.⁴²

The optical properties of mc-FeTiO₃/NS-TiO₂ heterostructures annealed at different temperatures and their components are shown in Figure 3a. FeTiO₃ shows strong absorption both in the UV and visible light range. The reported band gap energy of FeTiO₃ varies widely in the literature, but the value for bulk FeTiO₃ is generally reported to be between 2.5 and 2.6 eV.⁴⁷–⁵⁰ Values as high as 3.55 eV have also been reported for a FeTiO₃ thin film.⁵¹ The absence of a peak or edge in the UV–vis spectrum of FeTiO₃ relating to the bandgap excitation is explained by absorption from the intercalation charge transfer between Fe²⁺ and Ti⁴⁺ (and Fe³⁺ and Ti³⁺) that occurs at a lower energy.⁵²,⁵³

The heterostructured powders annealed at different temperatures show similar reflectance to each other in the UV and visible range. No significant difference for light absorption is observed. In addition, the reflectance of the heterostructured powders is more similar to FeTiO₃ than TiO₂. Combined with the XRD result that little Fe doping is observed in the TiO₂ coating, the similarity of the optical properties of mc-FeTiO₃/NS-TiO₂ heterostructures to FeTiO₃ indicates the mc-FeTiO₃ core is the primary light absorbing component in the heterostructure (though absorption in the coating cannot be ruled out). The Fe-doped TiO₂ powder (which is yellow in color) extends its absorption edge into the deep visible-light range and shows stronger absorption in both the UV and visible range than the undoped sample. The UV–visible absorption of PbTiO₃/TiO₂ and (Bi, La, Y)FeO₂/TiO₂ is shown in Figure 3b. The (Bi, La, Y)FeO₂/TiO₂ heterostructures showed stronger visible-light absorption than the materials with titane cores and absorbed light with wavelengths less than about 590 nm.

The physical properties of FeTiO₃/TiO₂ annealed at different temperatures and their reactivities for photocatalytic dye degradation of methylene blue are shown in Table 2.

<table>
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<tr>
<th>Catalyst</th>
<th>Processing Temp (°C)</th>
<th>BET Surface Area (m²/g)</th>
<th>Pore Vol (cc/g)</th>
<th>KₘB (h⁻¹)</th>
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<tr>
<td>TiO₂</td>
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<td>83</td>
<td>0.14</td>
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</tr>
<tr>
<td>FeTiO₃</td>
<td>500</td>
<td>0.47</td>
<td>0.003</td>
<td>0.03</td>
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<td></td>
<td>400</td>
<td>93</td>
<td>0.13</td>
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</tr>
<tr>
<td>FeTiO₃/ TiO₂</td>
<td>500</td>
<td>73</td>
<td>0.11</td>
<td>0.17</td>
</tr>
<tr>
<td></td>
<td>600</td>
<td>40</td>
<td>0.06</td>
<td>0.09</td>
</tr>
</tbody>
</table>

Figure 3. UV–visible spectra of (a) mc-FeTiO₃/NS-TiO₂ heterostructures annealed at different temperatures, its components, and Fe-doped TiO₂ and (b) PbTiO₃/TiO₂ as well as the ferrite/TiO₂ heterostructures annealed at 500 °C.
the core/shell structure, which demonstrates that the core/shell heterostructured powder is more active. In addition, the reactivity of mc-FeTiO$_3$/ns-TiO$_2$ and TiO$_2$ for methylene blue dye degradation in the dark is also presented in Figure 4. Little degradation was observed for the powders without irradiation, which confirms that the photocatalyst is stable in such conditions.

TiO$_2$ exhibits higher dye degradation rates under visible-light illumination than in the dark, even though it does not absorb visible light. This phenomenon is known as “TiO$_2$-mediated dye degradation” or “self-photosensitized degradation” of dyes.$^{54,55}$ In this process, TiO$_2$ is not excited to produce electrons and holes but only provides the pathway to transfer the injected electrons from the excited dye to an adsorbed dye molecule on the TiO$_2$ surface for degradation.

To test if the enhancement of the photocatalytic activity for mc-FeTiO$_3$/ns-TiO$_2$ originates from the interdiffusion of Fe to the TiO$_2$ coating, Fe-doped TiO$_2$ was prepared and tested for MB degradation under visible light. The previous literature reports that Fe doping can extend the absorption of TiO$_2$ to the visible-light range, which was also observed in our UV–vis experiments.$^{56}$ This has been suggested to arise from the creation of a donor level above the valence band edge; the donor level leads to absorption in the visible region, and thus, leads to photocatalytic activity enhancement for water splitting and some dye degradation experiments.$^{57,58}$ However, the substituted Fe dopants can also serve as centers for charge carrier recombination$^{59,60}$ which then reduces the overall photocatalytic activity. The current experiments demonstrate that 1% Fe doping did not enhance the photocatalytic activity of TiO$_2$ for MB degradation and implies that unintentional Fe doping of TiO$_2$ is not likely the cause of the high reactivity of mc-FeTiO$_3$/ns-TiO$_2$ heterostructured powders.

The influence of annealing temperature on the photocatalytic activity of heterostructured powders is shown in Table 2. mc-FeTiO$_3$/ns-TiO$_2$ annealed at 500 °C exhibits the highest reactivity for MB degradation among the three samples. The reactivity of the sample annealed at 500 °C (0.17 h$^{-1}$) is 4.3 times and 1.9 times that of the powders annealed at 400 °C (0.04 h$^{-1}$) and 600 °C (0.09 h$^{-1}$), respectively. It is noteworthy that the sample annealed at 500 °C is more reactive than the one annealed at 400 °C, even though it has a smaller surface area. These collected observations will be discussed further, after first presenting the results from the perovskite iron-oxides (AFeO$_3$).

The physical properties of AFeO$_3$/TiO$_2$ (A = Bi, La, Y) and PbTiO$_3$/TiO$_2$ are listed in Table 3. Compared to TiO$_2$ annealed at 500 °C, (Pb, Fe)TiO$_3$/TiO$_2$ shows low surface area, whereas (Bi, La, Y)FeO$_3$/TiO$_2$ displays high surface area. This phenomenon can be explained by a difference in the scaffold effect from the core to the microstructure of the nanostructured coating. Organic molecules are removed from the three-dimensional network of the xerogel during annealing and interparticle pores were formed. This is the origin of porosity of the nanostructured coating. The pore structure then begins to collapse with a further increase of temperature. The core can scaffold the pore structure, preventing the coating from collapsing to some degree and coating densification is decreased. In this case, (Bi, La, Y)FeO$_3$ cores resist coating densification better than (Pb, Fe)TiO$_2$ cores. The large pore volumes for (Bi, La, Y)FeO$_3$/TiO$_2$ support this view.

The visible-light reactivities of the photocatalysts synthesized for this work, measured by using the degradation of methylene blue, are shown in Figure 5 and listed in Table 3. The compounds with Fe on the B-site show less photocatalytic activity for dye degradation than those with Ti on the B-site. Although mc-BiFeO$_3$/ns-TiO$_2$ shows a slightly higher degradation rate than TiO$_2$ alone, mc-LaFeO$_3$/ns-TiO$_2$ and mc-YFeO$_3$/ns-TiO$_2$ have an even lower reactivity. All of the single component powders (mc-PbTiO$_3$, mc-FeTiO$_3$, mc-BiFeO$_3$, mc-LaFeO$_3$, and mc-YFeO$_3$) show little reactivity for methylene blue degradation. Their reactivities are far smaller than TiO$_2$ alone because of their small surface areas. This result also means the enhanced reactivity of some of the heterostructured...
powders originates from the interaction between core and shell, rather than the components alone.

4. DISCUSSION

The primary observation in this paper is that ATiO$_3$/TiO$_2$ (A = Pb, Fe) shows significantly enhanced photocatalytic activity under visible light irradiation when compared to their components alone, while AFeO$_3$/TiO$_2$ (A = Bi, La, Y) does not. This interesting phenomenon suggests that the B site in the ferrites: the positions of the band edges, internal polarizations, built in potentials from diodes, and O orbitals will experience less of a potential change at the interface than electrons in states formed from the overlap of Ti and O orbitals will experience less scattering. It should be noted that these estimates have uncertainties of at least 100 mV. Figure 6 compares the estimated band positions of the materials considered here relative to standard hydrogen electrode (SHE) level, which is defined as 0 eV. According to these estimates, all of the conduction band edges are below that of TiO$_2$ and they do not differ in energy by more than 620 mV. There is no obvious trend between the band edge positions and the reactivities of the heterostructures. In fact, there are no significant differences between the band edge positions of the compounds with Fe and Ti on the B-sites. The only notable correlation is that the compounds containing Fe on the B-site all have valence band edge positions that are above the positions of the titanates. This suggests that a larger hole transfer overpotential at the ferrite/titanate might limit the reactivity of the ferrite based materials.

It has previously been shown that the ferroelectrics can have enhanced photochemical response,$^{33,40}$ The internal field from the micrometer-sized ferroelectric cores can assist in the separation of photogenerated electrons and holes and thus improve the efficiency of the ferroelectric/TiO$_2$ heterostructures. Therefore, the compounds studied here were selected so that there would be ferroelectric and nonferroelectric examples of both the titanates and ferrites. Although the ferroelectric examples (PbTiO$_3$ and BiFeO$_3$) of each composition type degraded methylene blue faster than the nonferroelectric examples, the nonferroelectric titanate was better than all of the ferrites. Furthermore, BiFeO$_3$ supported titania is not significantly better than unsupported titania. On the basis of these findings, the ferroelectric properties by themselves cannot explain the trends in the photochemical reactivity of these heterostructures.

The presence of a p–n junction at the interface between the core and the titania coating will create and internal field that can separate photogenerated charge carriers and this will potentially increase the reactivity. Titania is n-type in all normal situations. However, both PbTiO$_3$ (n-type) and FeTiO$_3$ (p-type) have enhanced reactivities. The ferrites are all p-type and will form n-p junctions with titania, yet do not have enhanced reactivity. On this basis, the presence or absence of a p–n junction does not appear to be a dominant factor determining the relative reactivity of these compounds.

A final possible reason for the enhanced activity of the titanates is the continuity of Ti–O–Ti bonds across the ATiO$_3$/TiO$_2$ interface. This might reduce the barrier for transmission across the interface from where the carriers are generated (the core) to where they react with the solution (the titania shell). Both the Ti and Fe are octahedrally coordinated in the core (Fe and Ti) and shell (Ti). The bonding between Fe$^{3+}$ in the FeO$_6$ octahedra to Ti$^{4+}$ in TiO$_6$ octahedra will form Fe–O–Ti bonds, which changes the polarity compared to Ti–O–Ti interfacial bonds.$^{33}$ It is reasonable to assume that electrons occupying states in bands formed by the overlap of Ti and O orbitals will experience less of a potential change at the interface than electrons in states formed from the overlap of a Fe and O orbital, and thus experience less scattering. It should be noted that the pore volume and surface area of AFeO$_3$/TiO$_2$ are larger than those of ATiO$_3$/TiO$_2$ (Tables 2 and 3). The

Table 4. Electronic Properties of Various Core Materials and TiO$_2$ ($E_{bg}$ is the Band Gap Energy, $E_c$ is the Electron Affinity, $E_v$ is the Conduction Band Position, and $E_v$ is the Valence Band Position)

<table>
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<th>materials</th>
<th>$E_{bg}$ (eV)</th>
<th>$E_c$ (eV)</th>
<th>$E_v$ (eV)</th>
<th>$E_v$ (eV)</th>
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<tr>
<td>LaFeO$_3$</td>
<td>2.1</td>
<td>4.5</td>
<td>0</td>
<td>2.1</td>
</tr>
<tr>
<td>YFeO$_3$</td>
<td>3.2</td>
<td>4.6</td>
<td>0.1</td>
<td>2.2</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>3.2</td>
<td>4.1</td>
<td>−0.4</td>
<td>2.8</td>
</tr>
</tbody>
</table>

Figure 6. Schematic of band gap and band energy levels for the materials considered here.
denser coatings in the latter system may be the result of stronger bonding between ATiO₃ and TiO₂ than between AFeO₃ and TiO₂. The enhancement of reactivity of mc-FeTiO₃/nS-TiO₂ for methylene blue degradation with increased annealing temperature suggests that the interface quality and bonding between the core and shell are beneficial for the improvement of photocatalytic activity. Finally, it must also be noted that the structure of FeTiO₃ differs from the perovskite cores used in this study. FeTiO₃ takes the ilmenite structure and is made up of both FeO₆ and TiO₆ octahedra. Though both Fe³⁺/Ti⁴⁺ and Fe²⁺/Ti⁴⁺ pairs exist in FeTiO₃, FeTiO₃ still can be considered as one member of a series of compounds that includes the titanates A²⁺Ti⁴⁺O₃ and there will still be Ti–O–Ti bonds at the core–shell interface.⁵⁰,⁶⁴,⁶⁵

The idea that continuous metal–oxygen–metal bonds across the phase boundary promotes charge transfer is consistent with results from polymorphs of TiO₂ and Ga₂O₃. Bickley et al. suggested that the high reactivity of P25 titania is the result of absorption in an anatase core and then charge transfer to a thin rutile overlayer.¹⁵ Similarly, Wang et al. ascribed the high photocatalytic activity of α–/β-Ga₂O₃ composites to charge transfer between the two polymorphs.¹⁶ These past findings, together with the present results, suggest that when selecting materials to form a composite catalyst based on a semiconductor junction, both phases should have the same metal–oxygen bonds on either side of the interface.

One last physical characteristic of the materials that could affect reactivity is the charge carrier density, which was not controlled or quantified in these experiments. If the relatively high reactivity in the titanates derives from a space charge region at the interface between the two phases that separates charges and reduces recombination, then the width of this region would vary with the carrier density. So, if the ferrites systemically have a much higher concentration of carriers than the titanates, then these carriers would more effectively screen the charge at the core–shell interface, reducing the volume of the material in the space charge region where recombination is suppressed. This would lead to reduced reactivity in the materials with higher charge carrier density.

■ CONCLUSION

PbTiO₃/TiO₂ and FeTiO₃/TiO₂ heterostructures showed enhanced photocatalytic activities compared to their components while BiFeO₃/TiO₂, LaFeO₃/TiO₂, and YFeO₃/TiO₂ did not. The observation that catalysts with titanate cores showed enhanced reactivity while catalysts with ferrite cores did not is not simply correlated to energy level positions, built in potentials, or the presence of dipolar fields from ferroelectrics. The continuity of bonding at the interface between the titania core and the titania shell is the most likely explanation for the enhanced reactivity found in PbTiO₃/TiO₂ and FeTiO₃/TiO₂.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: gr20@andrew.cmu.edu. Fax: 412-268-7596. Tel: 412-268-2696.

Notes

The authors declare no competing financial interest.

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