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Life Cycle Impact of Titanium Dioxide Nanoparticle Synthesis through Physical, Chemical, and Biological Routes

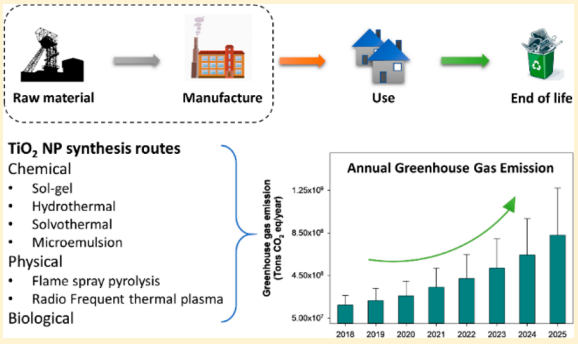
Fan Wu,*[,†] Zheng Zhou,[‡] and Andrea L. Hicks[†]

[†]Department of Civil and Environmental Engineering, University of Wisconsin-Madison, Madison, Wisconsin 53706, United States

[‡]Department of Chemistry and Biochemistry, Brigham Young University, Provo, Utah 84602, United States

Supporting Information

ABSTRACT: The sustainable manufacturing of nanoparticles (NPs) has become critical to reduce life cycle energy use and the associated environmental impact. With the ever-growing production volume, titanium dioxide (TiO_2) NPs have been produced through various synthesis routes with differing input materials and reactions, which result in differential reactivity, crystallinity, surface areas, and size distributions. In this study, life cycle assessment is used to analyze and compare the environmental impact of TiO_2 NPs produced via seven routes covering physical, chemical, and biological syntheses. The synthesis routes are chosen to represent mainstream NP manufacturing and future trends. Mass-, surface area-, and photocatalytic reactivity-based functional units are selected to evaluate the environmental impact and reflect the corresponding changes. The results show that impact associated with the upstream production of different precursors are dominant for the chemical route. Compared to the chemical route, the physical route requires substantial quantities of supporting gas and high-energy inputs to maintain high temperature; therefore, a higher environmental burden is generated. A high environmental burden is also modeled for the biological route due to the required bacterial culture media. This present study aims to identify the most efficient synthesis route for TiO_2 NP production, lower the potential environmental impact, and improve green synthesis and sustainability.



1. INTRODUCTION

Titanium dioxide nanoparticles (TiO_2 NPs) are one of the most promising photocatalysts due to their appropriate electronic band structure, photostability, chemical inertness, and commercial availability.[1,2] The wide application of TiO_2 NPs in numerous product fields, including cosmetics, solar panels, packaging, food, coatings, paints, pigments, textiles, filtration, and purification,[3−12] makes it the second most produced type of NPs over the past few decades. Due to the comparably low production cost and increasing need for high-grade TiO_2 NPs, the environmental impact of TiO_2 NP synthesis has become extremely crucial with respect to sustainable engineering and chemistry.[13] Previous research indicates that the projected TiO_2 NP production will continue growing exponentially and reach over 2 million metric tons by 2025.[14]

However, with the various routes of production techniques, the environmental impact of TiO_2 NP synthesis has not yet been systematically evaluated and compared. Life cycle assessment (LCA) is a systematic tool for determining the environmental impact (using metrics such as kilograms of carbon dioxide emitted) of a product or process across its entire life cycle or a portion of its life cycle.[15,16] Multiple studies conducted on nanoenabled consumer products using an LCA approach have identified NP manufacturing as an energy and environmentally intensive process that elicits significant environmental impact.[17,18] Thus, it is vital to investigate and identify the environmental impact generated during TiO_2 NP synthesis.

Current studies on nano-TiO_2-related LCA typically investigate a single synthesis method per study. Although several synthesis methods for TiO_2 production have been previously reported,[19−21] only seven synthesis methods have been studied for their life cycle impact (for both bulk and nanoscale TiO_2). The sulfate and chloride processes are two of the early stage procedures that produce TiO_2 pigment.[22] A newer TiO_2 manufacturing method has been reported to produce micron-sized TiO_2 using alkaline roasting of titanium slag (ARTS).[23] This procedure has produced commercial grade purity TiO_2 with reduced energy consumption and carbon footprint.[24] Four studies have focused on evaluating the environmental impact of TiO_2 NP production specifically using an LCA approach. Grubb et al. calculated the energy demand for an alternative Altair hydrochloride process (AHP) to produce TiO_2 NPs using ilmenite and hydrochloric acid,

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indicating that the energy consumption is similar to that of the sulfate process, although the AHP can produce nano-TiO_2.[25] Pini et al. carried out an LCA using SimaPro (v7.3.3) and the IMPACT 2002+ evaluation method for the hydrolytic sol−gel synthesis of TiO_2 NPs.[26] In this study, titanium isopropoxide (TTIP) and water were used in a bottom-up sol−gel synthesis to obtain a high-quality TiO_2 NP suspension (6 wt %) with a mean size of 30 nm. The study by Pini et al. identified that most impacts are produced due to the high energy demand for operating the process, including temperature, as well as the use of an organic precursor (an intermediate Ti compound used to synthesize TiO_2 NP) TTIP with a higher environmental impact. Caramazana-Gonzalez et al. used continuous flow solvothermal and hydrothermal syntheses and generated high-quality TiO_2 NPs from a wide range of organic precursors.[27] Five different organic precursors were assessed, where titanium oxysulfate (TIOS) had the lowest energy demand and global warming (GW) potential. Finally, a recent "green" supercritical fluid flow synthesis referred to using "green" solvents (only ethanol and water) and processing at moderate temperatures was investigated.[28] The LCA was conducted using openLCA (v1.6.3) and ReCiPe (v1.0.5) and suggested that the supercritical fluid flow had benefits from a cumulative energy demand (direct and indirect energy use throughout the synthesis life cycle) and climate change perspective compared to a conventional precipitation route. Although these synthesis techniques have been previously evaluated by LCAs, the lack of consistency with regard to the scope, assessment method, impact categories, and input materials considered during the analysis make it difficult to compare the sustainability and environmental impacts of these techniques under the same basis and across different studies.

Moreover, a very limited number of studies have evaluated the environmental impact of multiple NP synthesis procedures for cross comparison. Pourzahedi et al. investigated the environmental trade-offs of seven different silver (Ag) NP synthesis processes (four of which are chemical reduction methods with varying reducing agents),[29] and found the upstream production of bulk silver to be dominant for nearly every category of environmental impact and contributed over 90% of life cycle burdens in some cases. Stieberova et al. summarized the environmental impact and cost of multiple production technologies for 1 kg of TiO_2 NPs with respect to greenhouse gas emissions and energy demand.[30] This summary provides basic information on the setup cost, energy demand, and carbon dioxide emissions of TiO_2 production through a literature review; however, Stieberova et al.'s review lacks a major quantitative assessment for the synthesis procedures across multiple environmental impact categories. Therefore, establishing a systematic study to compare multiple TiO_2 NP synthesis processes under the same basis is urgently needed.

A previous study suggested that the production of NPs generated significantly greater environmental impact than other bulk chemicals.[31] Another study identified that NP production was the largest contributor to product impact throughout the life cycle.[32] In this study, a "cradle to gate" (from raw material extraction to manufacture) in-scope LCA focusing on seven different TiO_2 NP syntheses is conducted to evaluate their corresponding environmental impact to inform a cleaner synthesis and production. In addition, the present study aims to improve resource-intensive processes through the identification of the major impact contributions during the manufacturing stage of the TiO_2 NP life cycle. Synthesis routes, including physical/vapor (flame spray pyrolysis (FSP) and radio frequency (RF) thermal plasma), chemical/liquid (sol−gel, hydrothermal, solvothermal, and microemulsion), and biological synthesis processes, are chosen to represent the common TiO_2 NP manufacturing approaches and future trends. Although biological synthesis is not largely implemented in TiO_2 NP production, it has been recently developed using bacteria, yeast, fungi, and plants instead of toxic and expensive materials.[33,34] Research claims have suggested that such biological processes are green, eco-friendly, and sustainable for NP production.[35,36] Therefore, one representative biological synthesis method is selected to investigate the potential environmental impact and identify limitations in achieving cleaner production. This present study compares the environmental impact of seven synthesis procedures based on three different functional units: mass, surface area, and photocatalytic reactivity. Furthermore, the overall energy demand and GW potential are predicted according to the projected production volume of TiO_2 NPs from 2018 to 2025. Importantly, the inputs in the analysis are curated from various research studies published based on laboratory-scale syntheses due to a lack of synthesis information at the industrial scale, although industrial scale data captures realistic impacts and should be considered whenever possible. The data and results generated in this study are intended to benefit future NP research and green synthesis while also addressing data gaps in the existing life cycle inventories.

2. METHODS AND MODELING

2.1. Scope and Overview. In this study, seven different TiO_2 NP synthesis procedures were assessed for their life cycle impact. The system boundary and schematics of each procedure and precursors used are illustrated in Supporting Information (SI) Figures S1−S8, and the material and energy inputs are listed in SI Tables S1−S8. The goal is to (1) assess the environmental impact profile of different TiO_2 NP synthesis procedures from "cradle to gate"; (2) compare the assessment of seven different TiO_2 NP synthesis procedures to identify the current environmental impact; and (3) minimize the environmental impact of the TiO_2 NP synthesis process to ultimately achieve green synthesis.

The life cycle environmental and human health impacts were modeled using SimaPro software (version 8.5) with Ecoinvent and USLCI (U.S. Life Cycle Inventory Database) as inventories.[37,38] TRACI 2.1 (tool for the reduction and assessment of chemical and other environmental impacts) was used as the assessment method.[39] The midpoint categories considered include ozone depletion (OD, kg CFC-11 equiv), global warming potential (GW, kg CO_2 eq), smog (PS, kg O_3 eq), acidification (AC, mol SO_2 eq), eutrophication (EU, kg N eq), carcinogenic (HHC, CTUh), noncarcinogenic (HHNC, CTUh), respiratory effects (RE, kg PM2.5 equiv), ecotoxicity (EC, CTUe), and fossil fuel depletion (FF, MJ surplus). The reactions are assumed to occur in a closed reactor to eliminate the release of NPs, which is not considered in the current study. Coproducts and byproducts generated during the processes are assumed to be emitted to the technosphere. Combustion waste, such as carbon dioxide (CO_2), is, however, not captured before emission to the atmosphere.

2.2. Functional Units. One kilogram of TiO_2 NPs (mass-based) was selected as the functional unit for the initial assessment. However, the functional units of the NPs are highlighted to focus on the NP-specific effects.[40] Two unique

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Table 1. Summary of the Produced TiO_2 NPs in Size, Surface Area, Crystallinity, And Yield Using Different Synthesis Methods

synthesis environment	synthesis procedure	precursors	size (nm)Anatase/Rutile (mean)	specific surface area (m^2/g)	Anatase/rutile (A/R%)	yield(%)	ref
liquid phase	sol−gel	TIP→TTIP	15/12(14.9)	99.7	95% A/5% R	80	50
	hydrothermal	TIP→TTIP	10.4	149.8 ([a])	100% A	75.5	51,52
	solvothermal	TIP→TTIP	50 −100 (80)	19.5 ([a])	100% A	77.8	53
	microemulsion	TIP→TTBO	50	256	100% A	85	54,55
	Biological	TIOS→ $TiO(OH)_2$	24.6	62.8	90% A/10% R([b])	100([b])	35,36
vapor phase	flame spray pyrolysis	TIP→TTIP	22/11(20.2)	71/128 (79.6) ([a])	85% A/15% R	70	56,57
	radio frequent thermal plasma	TIP→TTBO	34.5/28.2(32.9)	31.6/39.4 (33.6)	75% A/25% R	86	58,59

[a]Indicates that the specific surface area was determined based on the particle size reported by assuming sphere and smooth in the particle shape and morphology. [b]Indicates the % crystallinity, and an ideal yield (100%) is assumed in biological synthesis. Abbreviations: TIP-titanium tetrachloride; TTIP-titanium isopropoxide; TTBO-titanium tetrabutoxide; and TIOS-titanium oxysulfate).

properties of utilizing TiO_2 NPs are their high adsorption capacity and strong photocatalytic activity, which are dominated by their surface area, size, and crystallinity.[41,42] Only the consideration of mass may not accurately estimate the impact of the TiO_2 NP syntheses impacts with respect to the utility of varying surface area and reactivity.[29] Thus, the impact outcomes were rescaled based on the particle surface area and photocatalytic reactivity to reflect the changes in the environmental impact when effect-based function units were applied. A surface area of 1000 square meters (m^2) of TiO_2 NPs was used to indicate the surface area-based impact.

The catalytic activity is mainly dominated by the crystallinity and size of TiO_2 NPs. Anatase and rutile TiO_2 junctions are shown to be more photocatalytically active than anatase or rutile alone.[43] The anatase phase is thermodynamically metastable and can be transformed exothermally and irreversibly to the rutile phase at 450 to 1200 °C depending on the nature and structure of the precursor and preparation conditions.[44,45] Although it is unlikely that anatase would be converted to rutile at an industrial scale, to minimize the independent variables in comparing the photocatalytic activity of TiO_2 NP, standard P25 Degussa TiO_2 NPs containing a 3:1 anatase and rutile ratio was used as a baseline for the photocatalytic reactions.[46] Based on the produced crystallinity of each method provided, additional energy was necessary to transfer the anatase to rutile until the final 3:1 anatase/rutile ratio was obtained. Then, a size-dependent photocatalytic activity relationship previously demonstrated by Xu et al. was used to rescale the impact categories.[47] The reaction rate was interpreted as the rate to degrade methylene blue at the same initial concentration. The size-dependent photocatalytic activity relationship is expressed in a first-order reaction:

$$k = -0.064(d) + 0.260 \quad (1)$$

where k is the reaction constant (min^{-1}) and d is the diameter of the TiO_2 NPs (nm).

2.3. Synthesis Procedures. Detailed synthesis methods and procedures are documented in the SI, and Table 1 summarizes all the details of each synthesis method analyzed in this research. Due to limited knowledge regarding the production yield for biological synthesis, an ideal condition was assumed where the yield was 100%. The potential environmental impact is evaluated and compared to the other synthesis routes. Several criteria are followed for the specific article selection to represent each synthesis method as follows: (1) the same/similar precursors are used; (2) the final products (TiO_2 NPs) are all identified as spherical with a diameter ranging from 10 to 100 nm; and (3) the specific surface area (or BET) has been reported; (4) the crystallinity (relatively) has been reported; and (5) the synthesis method has been highly cited. If the specific surface area was not reported from the original synthesis research, then eq 2 is used to calculate the surface area assuming an NP with spherical shape and smooth surface:

$$A = 6/(\rho \times d) \quad (2)$$

where A is the specific surface area (m^2/g), ρ is the density of the anatase (3.84 g/cm^3) or rutile (4.26 g/cm^3) phase, and d is the diameter of the synthesized TiO_2 NPs (nm).

2.4. Energy Inputs. Information on energy use and its environmental impact on various processes is demonstrated in SI Table S9, which was obtained from the share of U.S. electricity generated by each fuel source in 2017 (simplified). For heating and evaporating, the energy requirements for the operation obey the first law of thermodynamics, where the energy required to heat compounds to a certain temperature is calculated as

$$Q_{heating} = m \times Cp \times \Delta T \quad (3)$$

where m is mass (kg), Cp is the heat capacity of the targeting compounds (KJ/(kg·°C)), and ΔT is the difference in the temperature (°C) between the system and the ambient surroundings. For evaporating and drying the liquid from the solution phase,

$$Q_{drying} = \sum m \times Hv \quad (4)$$

where m is the weight of each compound in the mixture (kg) and Hv is the heat of vaporization of each compound (KJ/kg). Notably, the energy calculations using the above method do not account for the energy losses. The energy losses used in this study are listed in the assumption column for each synthesis method in the SI.

The energy required for calcination was adopted from a previous study using a rotary kiln (74.6 kW motor) for experimental calcination.[27] The total energy required for the calcination process is 14.8 MJ/kg TiO_2 (with 18% energy loss). In addition, 15.0 MJ/kg TiO_2 for calcination was previously reported by Reck and Richards.[48] Thus, 14.8 MJ/kg TiO_2 was used as the energy input for calcination in the synthesis procedures.

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Environ. Sci. Technol. 2019, 53, 4078−4087

2.5. Sensitivity and Uncertainty Analysis. Sensitivity is the influence that one parameter (the independent variable) has on the value of another (the dependent variable), which determines the output parameter percentage change when varying an individual input parameter, while all other parameters are constant.[49] Therefore, the sensitivities of biological growth media were assessed by varying a single parameter value (increase by 25%) to compare the corresponding change to the overall impact in each impact category. The potential environmental impact of each synthesis procedure was also calculated based on the 60% and 100% production yields to see the potential variations (60% and 80% for the biological route). In addition, the uncertainty of each synthesis method was analyzed using Monte Carlo simulations in SimaPro for 1000 runs to the 95th confidence interval to present the uncertainties of the unit processes in the Ecoinvent used in our LCA models.

2.6. Prediction of Future Emission Trends. The research indicates that in scaling up from the laboratory to industrial scale, the materials and energy consumption of nanomaterial production may be reduced by a factor of 6.5 times.[60] Simplified scale-up factors (SF) of 2, 4, and 6 are assumed and used to project the laboratory scale results to an industrial scale prediction. The lower and upper bounds of GW potential were obtained from the uncertainty analysis, and the high and low yields for TiO_2 NP production were included to represent the standard deviation. Detailed results and calculations are shown in SI Table S20−S24.

3. RESULTS AND DISCUSSION

3.1. Impact Assessment of the Precursors. The LCA conducted reflects the environmental and human health impact of seven different TiO_2 NP synthesis methods. Three types of titanium precursors were used in seven synthesis methods, along with two organic precursors (TTIP and TTBO) and one inorganic precursor $TiO(OH)_2$.

To better understand the impact of using different precursors in the TiO_2 NP syntheses, the environmental impact of producing 1 kg of each precursor was analyzed and compared in Figure 1 (details of the process contribution and values are presented in SI Figure S9 and Table S10). Overall,

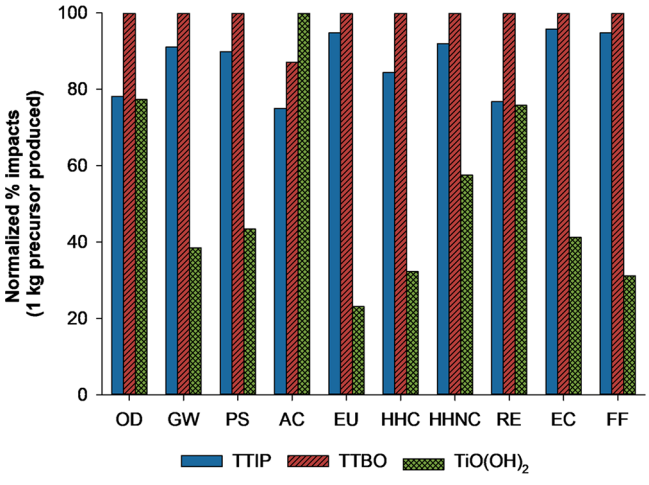

Figure 1. Impact comparison of three precursors used in this study. The contribution of each process in synthesizing the precursors is presented in SI Figure S9.

the organic precursors generated a higher impact than the inorganic precursor over nine impact categories except for AC, which was due to the use of H_2SO_4 when producing TIOS (SI Figure S9). Specifically, the impact of organic reagents contributed more than 50% in GW, PS, AC, HCC, and FF, where the production of first-generation precursors ($TiCl_4$/TIP and TIOS) dominated or contributed similarly to the reagents for the remaining categories (SI Figure S9). The main difference between TTIP and TTBO was the use of isopropanol or 1-butanol as the organic solvent. The amount of 1-butanol used for TTBO generated a higher impact than isopropanol across all impact categories (SI Table S11). The inorganic precursor ($TiO(OH)_2$) utilized input materials with a lower environmental impact when compared to the organic precursors. $TiO(OH)_2$ was achieved from a hydrolysis reaction of a first-generation precursor (TIOS), where the overall impact was less than $TiCl_4$ (first-generation precursor for TTIP and TTBO).[27] In addition, no organic reagent was used for producing $TiO(OH)_2$, and the Ti source (TIOS) and reagent (ammonia) consistently generated the majority of the impact on the overall production. Energy is not a contributing factor in the production of all three precursors.

The assessment conducted by Caramazana-Gonzalez et al. investigated the environmental impact of five different precursors, where titanium oxysulfate (TIOS) had the lowest energy demand and CO_2 emission.[27] TTIP, however, showed a much greater energy demand and CO_2 emission (40.3 and 73.7 kg CO_2-eq/kg TiO_2) than $TiCl_4$ and TIOS, based on the assumptions of the laboratory scale and temperature requirement. In addition, third- and fourth-generation precursors synthesized using TTIP considerably increased the greenhouse gas emissions and energy demand. Since many synthesis methods recently developed for manufacturing high grade TiO_2 NPs require organic precursors, such as TTIP and TTBO,[61] (with the exception of the biological synthesis methods), improvement over the production efficiency and reduction in the quantity of first-generation precursors and organic reagents required will potentially decrease the overall impact and energy demand for TTIP production.

3.2. Impact Assessment and Comparison of Seven Synthesis Methods. A comparison of the overall impact for the seven synthesis routes is demonstrated in Figure 2 and SI Table S12−S14. In addition, the environmental impact of each synthesis method and the associated uncertainties are shown in SI Figure S10. Based on the mass-based functional unit, physical routes have higher environmental impacts throughout all impact categories than chemical routes. The environmental impacts of synthesis methods follow the general trend: RF thermal plasma or biological (ideal case) > FSP > microemulsion > solvothermal > hydrothermal > sol−gel. RF thermal showed a high impact in the OD, PS, HHC, RE, EC, and FF categories, whereas the biological route dominated the other impact categories in GW, AC, EU, and HHNC. By excluding the RF thermal plasma and biological syntheses from the comparison (Figure 2), the analysis showed that manufacturing TiO_2 NPs synthesized by the FSP method with TTIP as the precursor sprayed in a methane−oxygen flame had the highest impact across all categories, except in OD, but especially in GW, PS, and AC. The high impacts in these three categories are due to the large quantity of CO_2 and NO gas emitted to the atmosphere through the combustion of organic solvents and gases. The microemulsion method had a higher OD impact than the other four methods (Figure 2 and

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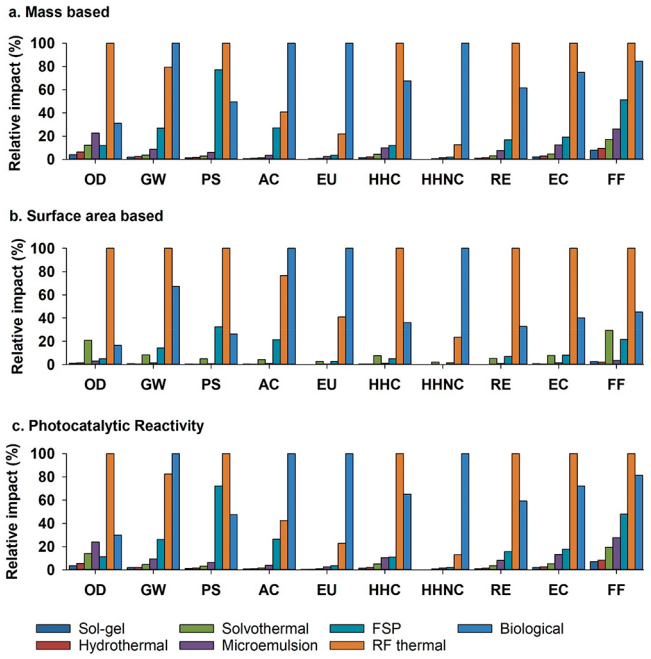

Figure 2. Relative environmental impact of all synthesis methods; normalization based on surface area and photocatalytic reactivity. Due to the large difference between the least and the most impact methods, a rescaled figure normalized based on the FSP method is presented in the SI, where the RF thermal plasma and biological synthesis routes are not included.

SI Figure S11), which is attributed to the consumption of the organic surfactant to create the water/oil (W/O) system. The major differences among the sol−gel, hydrothermal, and solvothermal methods are the use of chemical reagents during the synthesis. The sol−gel approach requires the least number of reagents, where TiO_2 NPs can be formed through the simple hydrolysis of the organic sol. Both hydrothermal and solvothermal methods require more reagents than the sol−gel method, including acids, large quantities of water and solvents, resulting in a higher environmental impact.

The RF thermal plasma, biological, and solvothermal routes incurred major changes in their relative environmental impact when the impact is rescaled based on their surface areas. Both RF thermal plasma and biological routes had a greater environmental impact than the other synthesis routes. For the RF thermal plasma, in addition to being highest in the OD, PS, HHC, RE, EC, and FF categories, the GW potential increased and became the highest among all synthesis routes (Figure 2b). When the RF thermal plasma and biological routes were not considered, the FSP method still showed a relatively high environmental impact on the selected impact categories (SI Figure S11b). The solvothermal method, surprisingly, showed a high impact in the OD, HHC, EC, and FF categories, even though the solvothermal approach had a relatively low impact under the mass-based functional units (SI Figure S11b). The changes are attributed to the larger size of TiO_2 NPs produced, which resulted in a smaller surface area. In contrast, the microemulsion route had a higher impact than the sol−gel, hydrothermal, solvothermal methods when using a mass-based functional unit (SI Figure S11a). Alternatively, when normalized by the surface area-based functional unit, the impact was significantly reduced due to the large surface area and highly monodispersed TiO_2 NPs synthesized (SI Figure S11b). The analysis suggests that the environmental impact of NP syntheses can be rescaled and significantly varied based on the specific NP application and functionality. For specific NP applications in relation to their surface area, such as the water treatment or purification where adsorption mainly depends on the contact available surface, this functionality is particularly relevant for consideration.[62]

Surprisingly, the environmental impact rescaled by the photocatalytic reactivity were not dramatically changed compared to the impact using mass-based functional units. The impact still followed the same trend as the mass-based results, with the RF thermal plasma and biological techniques being the most environmentally intensive methods and the sol−gel method being the least impactful method. However, small changes in some particular categories could still be observed. For instance, the OD category for the solvothermal, hydrothermal, and FSP methods showed a similar impact when the mass-based functional units were used, whereas the impact of the solvothermal method increased by 10−15% compared to the other two methods normalized by activity-based functional units (SI Figure S11a,c). The percent change between mass- and activity-based functional units in each synthesis method is shown in SI Table S15. The environmental impact of the sol−gel, hydrothermal, and FSP decreased from 3.1% to 13.3% across all impact categories. The solvothermal and microemulsion routes increased by 13.5% to 19.2%, and 5.9%t o 10.6% in all impact categories, respectively. The RF thermal method had a minimal increase in GW, AC, EU, and HHNC (<4%), whereas the biological route had a small decreasing impact in the selected categories (<4%). The changes in the rescaled impact in all categories are all within 20%. The minimum change in the impact is due to the low resolution of the size-reactivity relationship (eq 1) adopted. The size-reactivity relationship was calculated based on a wide range of selected samples (sizes of particles), where 49 μm, 11.6 μm, 6.1 μm, 3.0 μm, 2.4 μm, and 30 nm were chosen. In this study, only one nanosized TiO_2 was included during the experiment. The developed relationship when comparing microparticles and NPs might not be accurate enough to express the differences observed when all particles are below 100 nm. In other words, the relationship at the nanoscale lacks high resolution to significantly differentiate the changes in the environmental impact. Because some methods were several magnitudes higher than the other methods in some impact categories, even the highest change (19.2% in solvothermal route) was not able to significantly rerank the environmental impact outcomes of all synthesis methods. Taken together, the choice among these functional units was shown to change the rank order preference among the synthesis methods for all environmental impact categories considered. This ranking highlights the importance of adequate functional unit selection, ideally effect-based, for the environmental impact of nano-enabled product evaluation.

Figure 3 presents the relative contribution of different inputs and processes to the overall environmental impact categories. In general, the specific precursor contributed a high impact among all categories using the sol−gel (60.7−96.7%) and hydrothermal routes (48.8−79.4%) due to the low impacts from reagents and electricity. The main difference between the sol−gel and hydrothermal methods is the use of isopropanol or acetic acid. In addition, more acetic acid added as a reagent in the hydrothermal route contributed to a higher fraction of impact.

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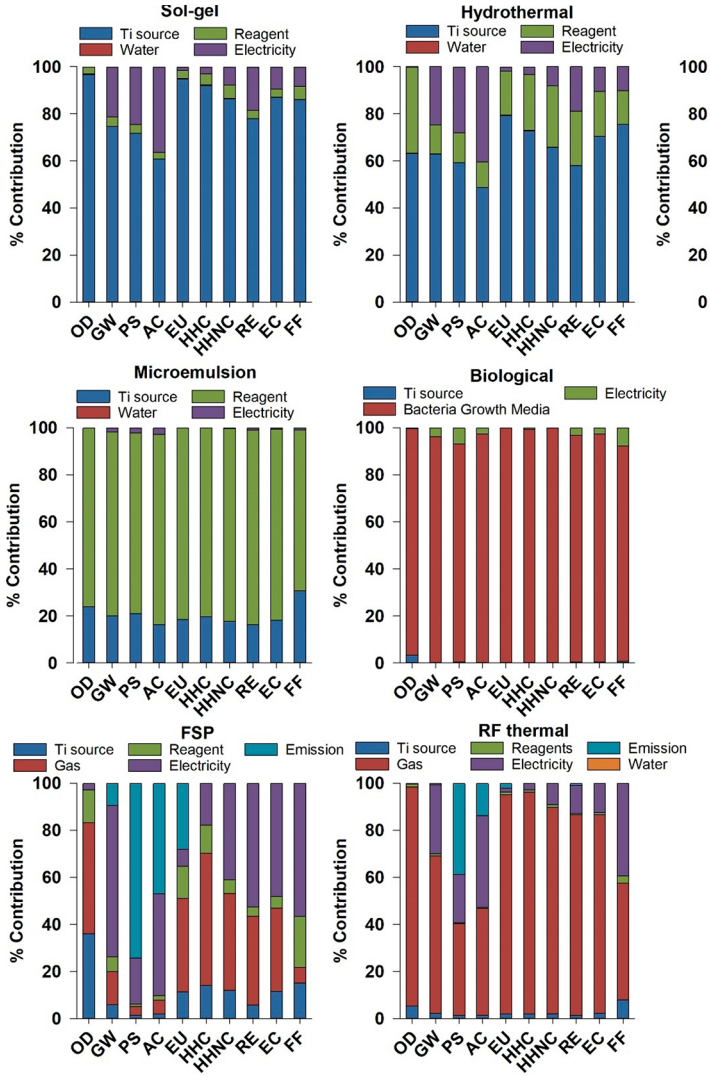

Figure 3. Reagent and process contributions to the overall environmental impact for the seven TiO_2 NP synthesis approaches.

Organic compounds used in the solvothermal and microemulsion methods contributed to over 50% and 70% across every impact category. Especially in the microemulsion route, three different organic reagents were used as surfactants and cosurfactants to create the W/O system. The energy required for heating was relatively low compared to other routes because NP drying was not needed when ethanol was used to washout and recover the particles from the oil phase.

The biological cultural media (MRS broth) contributed to the majority (over 91%) of the impact categories with regard to the biological route. The sensitivity around the MRS broth is largely due to the limited production information on the meat extract and peptone (SI Table S16 and 17). In this study, a 100% production yield was assumed; thus, the precursor $TiO(OH)_2$ was completely converted to NPs. However, the experimental procedure used only 20 mL 0.025 M (0.005 mol) $TiO(OH)_2$ in the 100 mL bacterial culture to generate TiO_2 NPs. To produce 1 kg TiO_2 NPs, approximately 2500 kg of bacterial culture media was required. Thus, increasing the conversion rate (the number of bacteria cells needed to convert the same quantity of the Ti precursors to TiO_2 NP) was the major challenge enhancing biological synthesis efficiency. Although Dhandapani et al. indicated that approximately 30−40% TiO_2 NPs by weight can be produced after 12 to 48 h using *Bacillus* sp. To deliver the nanomaterials, the NP production yield is still much lower using *Bacillus* sp. than that using the other synthesis methods. Moreover, the correlation of the bacterial density to the production rate is still unclear, making it challenging to comprehensively estimate the environmental impact of the biosynthesis. Future research focusing on improving the efficiency of the biosyntheses would be a major step in achieving "green" purposes.

For both physical routes, supporting gases (oxygen and methane for FSP, oxygen and argon for RF thermal plasma), electricity, and the emission from gas combustion are the three major impact sources. The TTIP precursor did not serve as a major contributor to these impact sources, with 5.7−15% in FSP (except 36% in OD) and less than 8% in RF thermal plasma. CO_2 and NO released to the atmosphere during combustion elicited high GW, PS, and AC potentials. Technologies related to combustion efficiency improvement and gas emission capture should be considered to reduce the potential impact. In addition, electricity (energy demand) is a large contributor for physical routes due to the use of energy-consuming heating plates, which has also been identified with other types of NP production, such as Ag NPs.[63]

Pini et al. previously conducted an LCA on a hydrolytic sol−gel method in producing TiO_2 NPs using the IMPACT 2002+

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Environ. Sci. Technol. 2019, 53, 4078−4087

method. Pini et al. suggested that heating during the process was the dominant contributor, whereas the organic precursor (TTIP) was only attributable to 13.65% of the total environmental impact. Differences in methods, scope, system boundary, functional units, and input materials are all potential reasons for the variation in the results obtained compared to this current work. Taken together, it is suggested that future research should focus on improving the production yield as a premise, optimizing the energy input, and switching to renewable energy sources to enhance the sustainability of TiO_2 NP production.

3.3. Cumulative Energy Demand. To add some context for comparison, the average energy consumption to produce 1 kg stainless steel (electric furnace) and titanium (Becher and Kroll processes) requires 75 and 361 mega joules (MJ) energy, respectively.[64] The cumulative energy demand (CED) is much higher for organic precursors; specifically, 220.7 MJ/kg and 240.3 MJ/kg were required for TTIP and TTBO production, respectively. The inorganic precursor $TiO(OH)_2$ required only 34.2% and 31.4% of the CED compared to TTIP and TTBO, respectively (Figure 4b and SI Table S18). To produce 1 kg

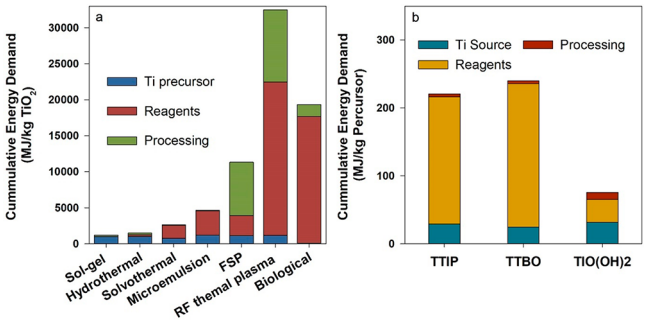

Figure 4. Cumulative energy demand for (a) each synthesis route of producing 1 kg TiO_2 NPs and (b) generating 1 kg Ti precursors (* biological route is assumed to produce 100% yield).

TTIP or TTBO, organic reagents contribute to the majority of the CED. When comparing all methods in Figure 4a, the CED follows a clear trend in the following sequence: RF thermal plasma > biological > FSP > microemulsion > solvothermal > hydrothermal > sol−gel. Reagents used in the RF thermal plasma, particularly argon gas, are the major contributors to the CED. In FSP, the use of oxygen and methane still contribute significantly to the CED, but the power used for the heating plate dominates the overall CED. The heating plate consumes a high quantity of energy for both physical synthesis routes.

Although biological synthesis appears to require less energy than the RF thermal plasma method, it is based upon the assumption of a 100% yield in the TiO_2 NP synthesis (Figure 4a and SI Table S19). With this premise, the CED for the biological process mainly depends on the amount of biological media utilized. The solvothermal and microemulsion methods are relatively less energy intensive due to a reduction in solvents and a lower required temperature. However, energy for organic reagent production is the major concern in terms of the CED. The sol−gel and hydrothermal methods again have the lowest CED, where TTIP consists of the largest portion of the energy consumption for synthesis. Caramazana-Gonzalez et al. indicated that the precursors can impact the results of energy demand due to fewer production steps during precursor manufacturing.[27] After comparing five different titanium precursors, titanium bis(ammonium lactate) dihydroxide (TiBALD), a third-generation precursor, has the highest CED values (1952−9157 MJ/kg TiO_2 depending on the synthesis temperature/conversion), whereas the CED significantly decreases to 102 and 149 MJ/kg for TIOS. Caramazana-Gonzalez et al. also assessed the energy demand of using TTIP as a precursor for the solvothermal synthesis, where approximately 1000 MJ/kg TiO_2 NP was required at 250 °C. However, the solvothermal method investigated here doubled the amount of the CED (2066 MJ/kg) due to the large quantity of organic reagent (1-butanol) used in the solvothermal approach, which contributed almost 67% of the total CED.

3.4. Prediction of GW Potential and Energy Consumption. With the increasing demand and applications for TiO_2 NPs, predicting the environmental impact and energy requirements associated with the projected production is crucial to the development of future synthesis methods. Research indicates that the majority companies use either vapor phase (43%) or liquid phase (42%) synthesis techniques in the industrial NP manufacturing processes.[65] Based on the predicted TiO_2 NP production volume from 2018 to 2025,[14] the GW potential (Figure 5) and the total CED (SI Figure

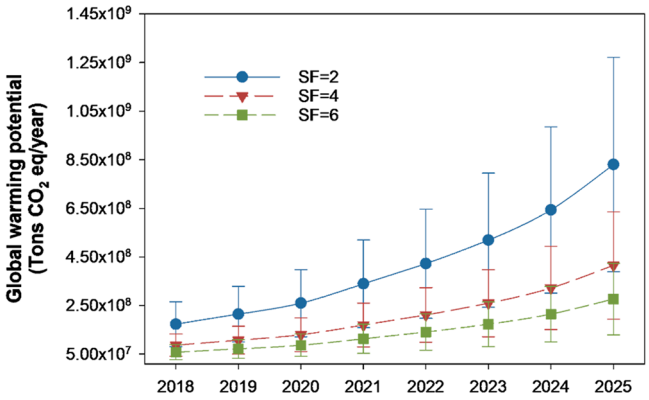

Figure 5. Predicted GW potential (tons CO_2 eq/year) using three different scale-up factors (SF) for TiO_2 NP production across the seven synthesis methods investigated in the current study. Error bars represent 95% confidence intervals for the uncertainties in the Ecoinvent unit processes and combined uncertainties of production yields.

S12) per year are estimated using the synthesis methods analyzed in this study (the results and detailed calculation steps are presented in SI Table S20). Upscaling from a laboratory-scale synthesis typically involves the development of mini-plant, pilot-plant, and then production-scale.[66] With higher reaction yields, the recycling of reagents and efficient equipment, the associated environmental impact and energy required for unit mass of TiO_2 NPs produced at the industrial scale are expected to be much lower than those at a laboratory scale,[67] and a screening level LCA may not accurately predict the environmental burdens by a direct scale up and the introduction of additional uncertainties.[68−70] With the assumed SFs, 5.76×10^7 to 1.73×10^8 metric tons of CO_2-eq is subjected to TiO_2 NP production in 2018 and are also projected to increase nearly five times in the next seven years. The GW potential predicted for 2018 from TiO_2 NP syntheses is equivalent to the emission of manufacturing 10−30 million

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Environ. Sci. Technol. 2019, 53, 4078−4087

standard gasoline vehicles.[71] For reference, 17.2 million lightweight automobiles were sold in the United States in 2018.[72] Although industrial-scale production is often optimized with respect to energy savings and waste treatments, the GW potential and CED associated with TiO_2 NP production still contribute significantly to the environmental impact. Greener technologies that utilize less energy and less environmentally impactful chemicals are the keys to improving the current environmental impact of NP manufacturing.

3.5. Discussion and Implications. At the "cradle to gate" level, current LCA studies performed on TiO_2 synthesis mainly aim to reveal the impact of a single synthesis method and to identify hotspots or portions of the life cycle with a significant environmental impact. These hotspots provide limited insight regarding the effect of the precursor and input information for a cross comparison of the environmental impact and energy demand. This work takes into account multiple environmental and human health impact categories, which provides a holistic assessment of the trade-offs of the different precursor materials and synthesis methods. By assessing the precursors used in this study, organic precursors require more energy for synthesis and cause a greater environmental impact, mainly due to the use of a substantial quantity of organic solvents. Physical synthesis routes are more energy intensive and more environmentally impactful. One common issue encountered in method is the limited characterization information on the synthesized TiO_2 NPs, which inhibits the selection for use in specific applications and raises questions regarding the functional equivalence of these TiO_2 materials. Thus, three different functional units were used to systematize and rationalize the comparison.

Nanospecific impacts from the potential release and exposure are not included in the current study, which have been largely overlooked in current nano-LCA studies. Only 8% of studies effectively quantified the eventual releases of NPs during the life cycle.[73] Specifically, four out of 14 LCA studies investigated nano-TiO_2-specific releases and impacts.[74−77] One study considered human health and ecotoxicity during production and waste release after production.[26] In this study, freshwater ecotoxicity was described as a new impact category using a calculated characterization factor, and the release of TiO_2 NPs in freshwater, which causes carcinogenic damage to human health, was introduced as a new calculated damage assessment factor. The overall impact of TiO_2 NP toxicity is extremely low in the study by Pini el al. because the damage is caused by the release of nano-TiO_2, and the unique Eco-design of this production method significantly limited the release of TiO_2 NPs. Due to the limited NP-specific impact assessments, the development of nanospecific characterization factors is critical to improve future nano-LCAs.

SI Table S25 summarizes the advantages and disadvantages of each method and estimates the corresponding environmental impact (GWP) and energy demand. However, environmental impacts should not be the sole criterion for the selection of TiO_2 NP production. Many other factors, including convenience, product quality (such as purity, size, shape, and functionality), cost, safety, processing time and equipment requirement, should also be considered to meet industrial needs. In general, chemical routes require less energy and generate less environmental impact, whereas the physical routes require considerable electricity and supporting gases, resulting in high GW impacts. Physical routes can produce NPs based on a variety of liquid precursors so that even noble metal-deposited TiO_2 can be synthesized in one step, which has great potential in industrial applications due to the simple procedures. NP production using biological synthesis has great potential due to its versatility and low cost. Moreover, research suggests that biological synthesis has the potential to directly attach varying surface proteins and functional groups based on the specific application of NPs while still within bacteria cells.[78] However, current research lacks information on the yield of the final products and consistency using biological approaches. In addition, major drawbacks associated with the biosynthesis of NPs using bacteria are tedious purification steps and a poor understanding of the mechanisms.[79] Therefore, the current strategy for the biological manufacturing of NPs remains at the development stage and laboratory scale. To reach industrial scale production, procedures should be improved with respect to energy input and conversion efficiency. Bioreactors may be applied to significantly enhance and control the growth of bacteria to increase the yield. In addition, the energy and materials required for the purification of endotoxin and biological waste should be considered for the overall assessment to achieve real "green" synthesis.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.8b06800.

Detailed synthesis information, flowcharts of synthesis procedures, life cycle inventory, comparative TRACI environmental impacts, comparative energy demand, uncertainty and sensitivity analysis, summary of the advantages and disadvantages of each synthesis procedure (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*Fan Wu: fwu64@wisc.edu.

ORCID

Fan Wu: 0000-0001-8621-9449

Zheng Zhou: 0000-0003-4960-0210

Andrea L. Hicks: 0000-0002-6426-9717

Notes

The authors declare no competing financial interest.

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