



Black TiO₂ Synthesis by Chemical Reduction Methods for Photocatalysis Applications

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Applications of TiO₂ nanomaterials in photocatalysis, batteries, supercapacitors and solar cells, have seen widespread development in recent decades. Nowadays, black TiO₂ have won attention due to enhancing the solar light absorption by the formation of oxygen vacancies and Ti³⁺ defects, to promote the separation of photo-generated charge carriers leading to the improvement of the photocatalytic performance in H₂ production and pollutants degradation. The enhanced photocatalytic activity of black TiO₂ is also due to a lattice disorder on the surface and the presence of oxygen vacancies, Ti³⁺ ions, Ti-OH and Ti-H groups. Enhancing the optical absorption characteristics of TiO₂ and change of energy level and band-gap of materials have been successfully demonstrated to improve their photocatalytic activities, especially for black TiO₂ nanoparticles, which promote visible light absorption. The current review focuses on the investigation of the chemical reduction synthetic route for black TiO₂ nanomaterials, and their proposed association with green applications such as photodegradation of organic pollutants and photocatalytic water splitting. The synthesis methods of black TiO₂ involves the changes from Ti⁴⁺ to Ti³⁺ state, into different strategies: (1) The use of highly active hydrogen species such as H₂, H₂/Ar or H₂/N₂ gases, and metal hydrides (NaBH₄, CaH₂), (2) the reduction by active metals such as aluminum, magnesium and zinc, and (3) organic molecules such as imidazole and ascorbic acid.

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THEORETICAL CONSIDERATION OF BLACK TiO₂

Chen et al. first reported black TiO₂ with a narrowed band-gap of 1.5 eV to expand the full spectrum sunlight absorption and promote an increase in the photocatalytic activity, by introducing surface disorders in the TiO₂ (Chen et al., 2011). Hu et al. observed in 2012 a remarkable enhancement in the visible-light absorption and the photocatalysis of TiO₂ after hydrogen treatment, attributed to surface disorder and the formation of oxygen vacancies (Hu, 2012; Wang and Chou, 2016; Zhu et al., 2016).

In the past decade, a considerable effort has been committed to preparing black TiO₂ by introducing Ti³⁺ defects and oxygen vacancies into the titanium oxide lattice (Di Valentin et al., 2009; Su et al., 2014; Li et al., 2015; Tian et al., 2015; Xin et al., 2015). Oxygen vacancy and Ti³⁺ defects are more detectable in black TiO₂ compared with white TiO₂. Oxygen vacancies have been detected by a few techniques (Zhang and Park, 2017): electron paramagnetic resonance (EPR), electron spin resonance (ESR), and Raman spectroscopy. Ti³⁺ defects are not proved in white

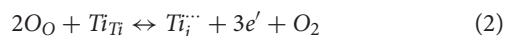
TiO₂, but they are detected in black TiO₂ based on X-ray photoelectron spectroscopy (XPS), by EPR (Jedsukontorn et al., 2017) or ESR spectroscopy (Tian et al., 2015). The yellow TiO₂ synthesis at a low temperature had more oxygen vacancies and Ti³⁺ defects compared with white TiO₂, which decreases the band-gap from 3.1 to 2.9 eV (Bi et al., 2020).

The formation defects in titanium oxide are given below (Jayashree and Ashokkumar, 2018):

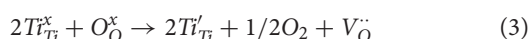
Oxygen vacancy (Kröger-Vink notation $V_{\text{O}}^{\cdot\cdot}$) formation at a low oxygen pressure



Titanium interstitials Ti³⁺ (Kröger-Vink notation $Ti_i^{\cdot\cdot}$):



Cui et al. (2014) described the generation of the Ti³⁺ and oxygen vacancies, by the equation of the defect (equation 3). They observed that the number of oxygen vacancies is half of the Ti³⁺ sites (equation 3). The absorption increases with the density of Ti³⁺ or O vacancies, as the density of Ti³⁺ increases with the Al reduction in temperature.



The colorful TiO₂ with better absorption properties and improved photocatalytic activities compared with white TiO₂ have been designed through (i) metal doping in which metal replaces Ti⁴⁺ ions in the TiO₂ lattice (Chen et al., 2015), (ii) non-metal doping to replace O²⁻ ions in the TiO₂ lattice (Hamilton et al., 2014), (iii) to replace partial Ti⁴⁺ and O₂ ions in the TiO₂ lattice. To replace Ti⁴⁺ in TiO₂ with any cation is more accessible than to substitute O²⁻ with anions (such as nitrogen, carbon, sulfur) due to the difference in the charge state and ionic radii (Lee et al., 2014).

The structural modifications in black titanium oxide, involving Ti³⁺ centers and oxygen vacancies, conduct significant changes in crystallinity, and optoelectronic as well as the surface properties, and the most marked effect is the color changing. Increasing the optical absorption properties and diminishing electron-hole recombination of TiO₂ are expected to be meaningful for excellent photoactivity.

The optical band gaps of white anatase and rutile TiO₂ are reported as 3.2 and 3.0 eV, respectively (Haider et al., 2019), that means TiO₂ can adsorb only the UV part of the solar spectrum. A significant reduction in the TiO₂ band-gap around 1.23 eV and optical absorption near 1,000 nm in the near-infrared region (Ullattil et al., 2018), has been reported by hydrogenation of anatase nanocrystals under pressure resulting in the black TiO₂ materials (Chen et al., 2011; Liu et al., 2013).

The color change of titanium oxide from gray, blue, brown or black color, reflects in turn the optical properties and structural changes (Yan et al., 2017). By exposure to visible light, a heterojunction type I (Isac et al., 2019) is formed between white TiO₂ and colored TiO₂, the band energy levels of colored TiO₂ are included in that of the white TiO₂, and both heterojunction

semiconductors could be excited to produce electrons and holes (Figure 1).

The colored TiO₂ shows a light absorption around 2eV, by introducing oxygen vacancies ($V_{\text{O}}^{\cdot\cdot}$) and Ti³⁺ formation into TiO₂ lattice (Naldoni et al., 2019) or introducing disordered layers in the surface of crystalline TiO₂ (Song et al., 2017) enhanced solar light adsorption and served to prove their photocatalytic performance. The oxygen vacancy can significantly affect the electric and optical properties of the materials, by forming a donor level below the conduction band, located at 1.8eV below conduction band of titania as shown in Figure 1. The Ti³⁺ defect is responsible for changes in the electronic conductivity and optical properties. The Ti³⁺ and $V_{\text{O}}^{\cdot\cdot}$ defects can be created by the reduction of TiO₂, either electrochemically, or through gas annealing and exposure in a vacuum (Lee et al., 2014).

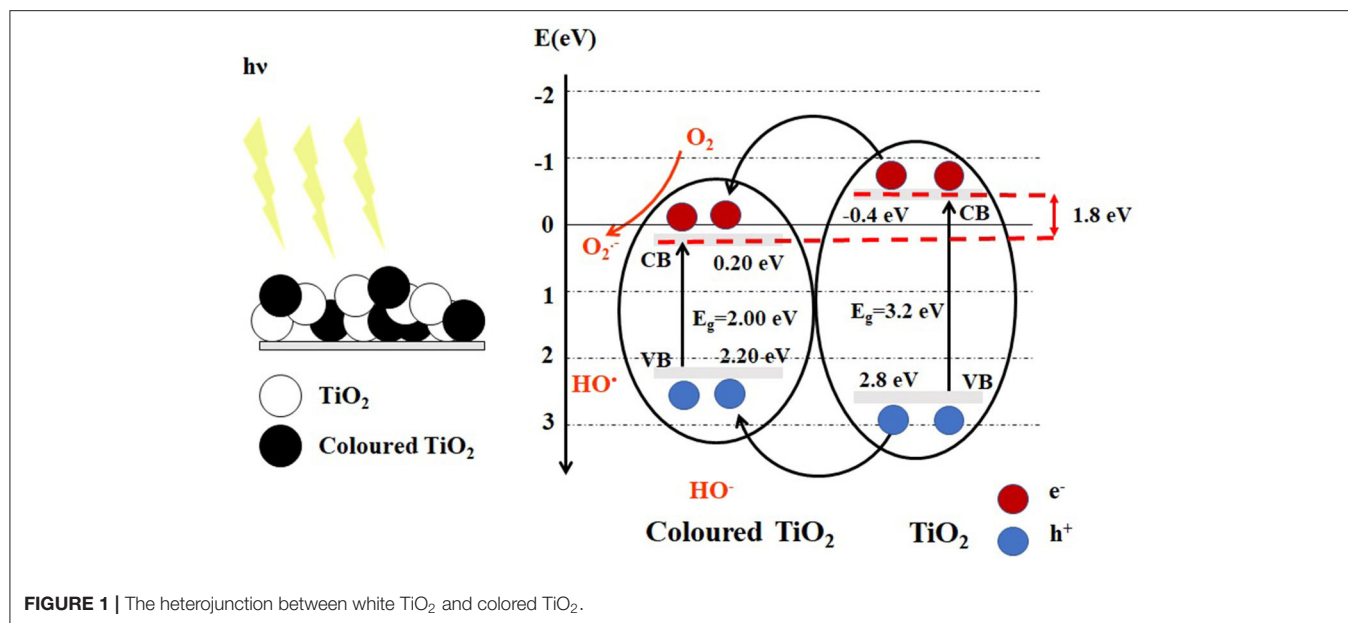
Hu emphasize the importance of the crystalline phase of titanium oxide in the synthesis of black TiO₂; the rutile phase is theoretically easier to obtain than anatase crystalline phase because the formation energy of an oxygen vacancy in the rutile surface (110) is lower (5.5eV) than in the anatase surface (001) (7.54 eV) (Hu, 2012). The most common phase of the black TiO₂ is rutile or anatase; the rutile phase is formed at a temperature below 500°C. The oxygen deficiency and amorphous surface of TiO_{2-x} were also reported by Tan et al. (2014). The photocatalytic behavior of TiO₂ was found to depend on the crystalline phase; the white TiO₂ anatase phase has been shown to have higher photocatalytic efficiency than rutile TiO₂. Contrary to the previous statement, black rutile TiO₂ has been reported to have the best photocatalytic performance.

The synthesis methods of black TiO₂ are significantly affected by the structural, morphological and optical properties; involving the changes from Ti⁴⁺ to Ti³⁺ state, into different strategies, (i) the use of highly active hydrogen species such as H₂, H₂/Ar or H₂/N₂ gases, and metal hydrides (NaBH₄, CaH₂), (ii) the reduction by active metals such aluminum, magnesium and zinc, (iii) organic molecules such as imidazole and ascorbic acid, have been confirmed to be capable of reducing white TiO₂ to black titania.

SYNTHESIS APPROACH OF BLACK TiO₂ BY CHEMICAL REDUCTION

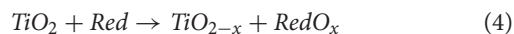
The synthesis methods explored through hydrogenation, plasma, chemical reduction, electrochemical reduction, laser ablation in liquid, and oxidation approaches were available in the literature over the last decade for black TiO₂ photocatalytic materials (Rajaraman et al., 2020).

The synthesis route influences the physicochemical properties and photocatalytic performance of black TiO₂. A significant number of studies highlight the formation of black TiO₂ by hydrogen thermal treatment when the samples had surface and bulk defects comparing with plasma treatment under Ar (95%)/H₂ (5%) atmosphere where the bulk defects were revealed (Wang and Chou, 2016). The color of the samples turned brown at 400°C, while the samples turned black at 500°C. The white TiO₂ Degussa powder was unchanged under hydrogenation,



emphasized the role of precursors and synthesis route (Leshuk et al., 2013).

The reduction strategy can be generally explained in Equation 4, where Red represents the reductant:



The noble gas atmosphere has been considered as reductant due to defective TiO_{2-x} formation in argon, nitrogen atmosphere, and the disordered layer forms only if crystallization is performed in an oxygen-free environment (Tian et al., 2015).



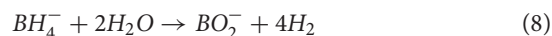
The first synthesis of black titanium oxide consists of anatase nanoparticles through treating white TiO₂ nanoparticles (precursors, titanium tetra-isopropoxide, ethanol, hydrochloric acid, deionized water, and Pluronic F127 as an organic template) under a 20.0-bar H₂ atmosphere at about 200°C for 5 days (Chen et al., 2011).

NaBH₄ Reduction

By reducing hydrides, black titanium oxide can be obtained through three approaches: (i) physical mixing of white TiO₂ and hydride, followed by annealing in an inert atmosphere (Ar, N₂) at temperature of 300...400°C, (ii) hydrothermal synthesis (Ren et al., 2015) and (iii) sol-gel process (Fang et al., 2014).

The sodium borohydride (NaBH₄) is a commonly used reducing reagent (Table 1), due to its ability to reduce Ti⁴⁺ to Ti³⁺, as in Equations (6) and (7), and to produce *in situ* active H₂ at room temperature, that reduces the white TiO₂ into black TiO₂ (Equation 8). During the NaBH₄ reduction process, boron oxide species are produced due to their insolubility in the ethanol, and it can be easily washed out by HCl solution to remove the surface impurities and expose the color centers on the surface of

the catalyst, significantly increasing the visible light absorption. The degradation efficiency increases 9 times after washing with HCl solution (Fang et al., 2014).



The rate of the generation of H₂ is higher in acidic conditions at experiments performed at 25°C with 20 g water per gram of sodium borohydride, and a wt. ratio accelerators/NaBH₄, around 1. The representative acidic materials that act as accelerators are tartaric acid, citric acid, succinic acid, oxalic acid (85...98% hydrogen liberated after 3 min), ammonium carbonate, maleic acid, aluminum sulfate, sodium diacid phosphate (90...80% of H₂ after 10 min), maleic anhydride, ammonium chloride, benzoic acid (80...65% of H₂ after 10 min). The catalytic effect of metals salt (cobalt, aluminum) was also demonstrated (Schlesinger et al., 1953).

The treatment of the TiO₂ nanotube in NaBH₄ for a short time (20–40 min) reduced the surface of TiO₂ into Ti³⁺, and introduced an oxygen vacancy that creates localized states, producing a narrower band-gap of 2.46 eV, which extends its optical absorption to the visible region comparing with 3.09 eV for pristine TiO₂ nanotubes (Table 1) (Kang et al., 2013). The films show good stability and excellent reproducibility of the samples.

Tan et al. report a solid-state chemical reduction of TiO₂ at mild temperatures (300–350°C), for different times up to 1 h, an approach for large-scale production for visible light photocatalysis and solar-driven H₂ production (Table 1). The preparation of black TiO₂ followed the procedure: 4 g of TiO₂ Degussa P25 powder was mixed at room temperature with 1.5 g of NaBH₄ (98%) and heated in a tubular furnace under Ar

TABLE 1 | The chemical reduction synthesis methods, properties and photocatalytic applications of representative black TiO₂ materials.

Materials		Applications		References
Synthesis	Characterization	Experimental	Photocatalysis efficiency	
NaBH₄ reduction				
<i>TiO₂ sol-gel synthesis</i> : Solution A: 5 mL tetrabutyl titanate and 25 mL EtOH. Solution B: 4 mL HNO ₃ (0.6 M) and 5 mL EtOH <i>NaBH₄ reduction</i> : NaBH ₄ add in the sol 0.025, 0.05, 0.1, 0.3 and 0.4 g	<i>Phase</i> : anatase, D= 9...35 nm <i>Band-gap energy</i> : 2.87 eV <i>BET surface area</i> : 18...27 m ² /g for black TiO ₂ (pristine: 2 m ² /g)	Rhodamine B 10 mg/L Catalyst 1 g/L <i>Light source</i> : 500 W tungsten halogen lamp, filter ($\lambda > 420$ nm), 300 W high-pressure Hg lamp, filter ($\lambda < 365$ nm)	<i>Degradation efficiency</i> : 100% after 5 h (sample 0.1-TiO ₂). The degradation rate increase 9 time after washing with HCl.	Fang et al., 2014
<i>TiO₂ synthesis</i> : anodic oxidation of titanium foils, annealed <i>NaBH₄ reduction</i> : nanotube arrays were dipped in 0.1 M NaBH ₄ for different times at room temperature	<i>Phase</i> : anatase, rutile and brookite <i>Morphology</i> : nanotube ~7 mm, pore diameter ~ 100 nm <i>Band gap energy</i> : 2.46 eV, (pristine 3.09 eV)	TiO ₂ (working electrodes), Pt (counter-electrode), Ag/AgCl (reference electrode). <i>Light source</i> : 300 W Xe lamp, UV cut-off filter of 420 nm, light intensity 0.37 W cm ⁻²	<i>H₂ production rate</i> : 1.31% at 0.40 V _{RHE} after 40 min (pristine 0.32% at 0.48 V _{RHE})	Kang et al., 2013
<i>TiO₂@TiO_{2-x} synthesis</i> : 4.0 g of Degussa TiO ₂ powder, 1.5 g of NaBH ₄ , heated to 300–400°C, Ar, 5–60 min, dark blue TiO ₂ 300°C/50 min	<i>Phase</i> : Anatase, rutile <i>Morphology</i> : core-shell <i>Band-gap energy</i> : 1.1...2.1 eV (pristine 3.1 eV) <i>BET surface area</i> : 43...50 m ² /g for black TiO ₂ (pristine: 45 m ² /g)	Methyl orange 20 ppm (V=50 mL, pH=1), Catalyst 1 g/L	<i>Degradation efficiency</i> : 90% after 10 min (Pristine 75%)	Tan et al., 2014
<i>TiO₂ synthesis</i> : hydrothermal TiCl ₄ , ethylene glycol, heated at 150°C/6 h <i>Defective TiO_{2-x} synthesis</i> : dual-zone tube furnace, Ar, 500°C/1h, TiO ₂ :NaBH ₄ mass ratio of 1 to 4	<i>Phase</i> : low crystallinity	Methanol (120 mL, 25%), Catalyst 50 mg/1 wt%Pt <i>Light source</i> : 300 W Xe lamp, UV cut-off filter of 400 nm	<i>H₂ production rate</i> : 6.5 mmol·h ⁻¹ ·g ⁻¹ (7.2 times better than pristine)	
		Methanol (30 mL, 10%) Catalyst 0.03 g/0.03 wt% Rh <i>Light source</i> : 500 W mid-pressure Hg lamp and a 420 nm cut-off filter	<i>H₂ production rate</i> : 580 mmol·h ⁻¹ ·g ⁻¹	Xu et al., 2019
Metal reduction				
<i>Reduced TiO_{2-x} synthesis</i> : Aluminum reduction into two zones tube furnace, $p < 0.5$ Pa, Al heated at 800°C, and TiO ₂ heated at 300... 600°C, 6 h and 20 h Annealing: 500...900°C, 12h, Ar	<i>Phase</i> : anatase, rutile, highly crystalline <i>Morphology</i> : core-shell, ~25 nm in diameter <i>Band gap energy</i> : ~3.2 eV similar to pristine <i>BET surface area</i> : 42 m ² /g (pristine: 43 m ² /g)	Methyl orange 0.1 M (100 mL) Phenol 0.3 M Catalyst 1 g/L	<i>Degradation efficiency</i> : 52% MO (4% pristine) after 6 h 78% Phenol (82% pristine) after 3.5	Wang et al., 2013
		Methanol 25% (120 mL) Catalyst (0.5 wt% Pt) 0.8 g/L <i>Light source</i> : UV irradiation: 300 W Hg lamp	<i>H₂ production rate</i> : H ₂ 6.4 mmol h ⁻¹ g ⁻¹ (8.5 times higher than that of pristine TiO ₂ (0.75 mmol h ⁻¹ g ⁻¹))	
<i>TiO₂ hollow sphere synthesis</i> : 1 mmol tetrabutyl titanate, 0.5 g carbon spheres, stirred for 6h, washed and dried at 90°C for 6 h. Annealing: 400–500°C, 4 h. <i>Black TiO₂</i> : Aluminum two-zones tube furnace, TiO ₂ 500°C zone, Al 800°C zone. Annealing: 6 h	<i>Phase</i> : high crystalline, D~8 nm anatase, rutile (>500°C) <i>Morphology</i> : Hollow sphere <i>Band gap energy</i> : <i>BET surface area</i> : 168.8 m ² g ⁻¹	Methanol 10% (100 mL) Catalyst: 0.2 g/L <i>Light source</i> : 300 W Xe-lamp band-pass filter ($\lambda = 365$ nm)	<i>H₂ production rate</i> : 56.7 mmol·h ⁻¹ ·g ⁻¹ , 2.5 times higher than pristine	Song et al., 2017
<i>Reduced TiO_x (x < 2)</i> nanoparticles (white, gray, blue, and black) were prepared by reducing P25 TiO ₂ (400 mg) with Mg (60...400 mg). Annealing: 600°C, 4 h, Ar.	<i>Phase</i> : TiO _{0.89} , TiO ₂ anatase TiO ₂ rutile, D ≈24 nm (as pristine) <i>Morphology</i> : core-shell	<i>Light source</i> : solar-simulated light irradiance at an intensity of 1000 W m ⁻² (1 Sun).	<i>Solar thermal conversion efficiency</i> : Black TiO _x : 50%	Ye et al., 2017

(Continued)

TABLE 1 | Continued

Materials		Applications		References
Synthesis	Characterization	Experimental	Photocatalysis efficiency	
Organic molecules reduction				
<i>TiO_{2-x}</i> hydrothermal synthesis: L-ascorbic acid (0, 0.3 g and 0.7 g), 70 mL DI water, 3.1 mL of TiCl ₃ , NaOH solution (1 mol/L) to pH=4. The mixture was transferred to a 100 mL Teflon-lined stainless steel autoclave and heated at 180°C for 12 h.	Phase: Anatase D=10...50 nm Morphology: core 10...50 nm Band gap energy: 1.0 eV BET surface area: 64.56 (white), 188.75 (brown), 263.95 m ² g ⁻¹ (black), respectively	Methylene blue (MB) 20 mg/L (V=40 mL) Phenol 10 mg/L Photocatalyst 0.5 g/L Light source: 300 W Xenon lamp, UV cut-off filter (λ > 420 nm)	Degradation efficiency: MB 90% (black TiO _{2-x}), 70% (brown TiO _{2-x}), 50% (white TiO _{2-x}), 5% (pristine), after 100 min Phenol 100% (black TiO _{2-x}), after 80 min	Wajid Shah et al., 2015

atmosphere, up to 300°C and held for 5–120 min. When the temperature increase to 350°C, the black titanium oxide was obtained in 60 min. The colored powders from light blue to black were washed with deionised water and ethanol several times to remove unreacted NaBH₄ and dried at 70°C (Tan et al., 2014).

Xu et al. obtained black TiO₂ powders in a dual-zone quartz tube furnace using titanium oxide synthesized of TiCl₄ and ethylene glycol at 150°C for 6 h in a Teflon-lined stainless-steel autoclave with NaBH₄ as reductant agent (Table 1). The reduction was carried out in an argon atmosphere, between 200 and 500°C for 1 h. The presence of Ti³⁺ and oxygen vacancy defects significantly increased the intensity of the band absorption in the visible spectrum range (Xu et al., 2019).

Metal Reduction

In recent studies, active metals such as magnesium, lithium, aluminum and zinc were used for the synthesis of black TiO₂ with oxygen-deficient metal oxides (Zu et al., 2019).

Ou et al. developed a room-temperature lithium reduction strategy removing oxygen, and generating oxygen vacancies into the titanium dioxide nanoparticles lattice. Lithium metal with a high reductive capacity can reduce a significant number of metal oxides at room temperature (TiO₂, ZnO, SnO₂, CeO₂). TiO₂ Degussa P25 and lithium powders (0...5% wt%) were mixed with a dispersant (dimethyl carbonate), then washed with diluted hydrochloric acid to remove lithium oxide, centrifugate and washing. The dried powders appear in different colors ranging from blue to black, and shift with the increase in lithium content (Ou et al., 2018).

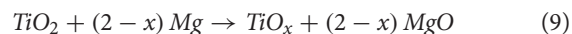
The aluminum reduction of titanium oxide produces black TiO₂ in two ways: (i) reduction approach in an evacuated two-zone vacuum furnace, low temperature (300–600°C) for TiO₂ and high temperature (800°C) for aluminum and (ii) thermal treatment of a mixture of TiO₂ and aluminum powder (Table 1) (Wang et al., 2013). The black TiO₂ nanotube arrays have been used as a photoanode of photoelectrochemical cells for water-splitting, which was about 5 times higher than that of pristine (Cui et al., 2014).

Song et al. Herein prepared the black TiO₂ nanoparticles through subsequent Al reduction, with hollow nanosphere morphology, high crystallinity, small grain size (~8 nm), and high surface area (168.8 m²·g⁻¹) for photocatalytic hydrogen

generation (56.7 mmol h⁻¹·g⁻¹) 2.5 times higher than pristine TiO₂ nanostructures. The aluminum reaction was performed for 6 h in an evacuated two-zone furnace, pristine TiO₂ hollow nanospheres were placed in the low-temperature zone (400...600°C), and the aluminum powder was placed at 800°C (Table 1) (Song et al., 2017).

Sinhamahapatra et al. report in 2015 a magnesiothermic reduction under a 5% H₂/Ar atmosphere followed by acid treatment to synthesize reduced black TiO₂ nanoparticles with improved optical absorption in the visible and infrared region for enhanced photocatalytic hydrogen production in the methanol-water system in the presence of Pt as a co-catalyst (Sinhamahapatra et al., 2015).

Nanoparticles with different colors were synthesized by Ye et al. (2017) using Mg as a reductant (Table 1). Commercial P25 TiO₂ nanoparticles were mixed with Mg powder into wt. ratio 20:3, 10:3, 5:3, and 1:1, before being purged with argon for 15 min and calcined at 600°C under an Ar atmosphere for 4 h. The TiO_x (x<2) nanoparticles with different Ti/O ratios increased with the increasing addition of Mg in the reaction (Equation 9) and colors (turned gray, blue-gray, light black, and dark black, respectively). The nanoparticles are material for converting solar energy to the thermal energy for evaporation of water.



Organic Molecules Reductant

Seok et al. synthesis Ti³⁺ self-doped TiO₂ using the sol-gel route: 5 g of TiOSO₄, 250 ml distilled water, 1.5 g urea as a dispersant, NaOH was added (pH=7), and precursors annealed under an oxidative atmosphere at 350°C for 6 h in the presence of 2-methylimidazole and HCl when the Ti⁴⁺ was reduced to Ti³⁺ which resulted in lower internal resistance and improved electronic conductivity with application in Li-ion batteries as anode materials with a capacity retention of 88% at 50°C (Seok et al., 2016).

A facile hydrothermal approach, described in Table 1, has been developed by Wajid et al. to prepare defective TiO_{2-x} high surface nanocore using ascorbic acid as a reductant, established the oxygen vacancy concentration and tunable band-gap by setting the amount of ascorbic acid (Wajid Shah et al., 2015).

The synthesis methods of black TiO₂ changed the phase and crystallinity, morphology, band-gap and BET surface area, essential elements in photocatalysis as described in **Table 1**. The experimental conditions (pollutants and catalysts concentration, light irradiation and intensity) influence the pollutant degradation efficiency and H₂ production rate by photocatalysis (**Table 1**).

The synthesis techniques to obtain black TiO₂ and defective TiO_{2-x} follow four strategies: introducing surface disorders, Ti³⁺ defects, oxygen vacancies, Ti-OH and Ti-H groups to narrowing the band-gap for photo-related applications (Liu et al., 2017; Yan et al., 2017).

Chemical reduction is associated with a change in the oxidation state of Ti⁴⁺ with the formation of Ti³⁺ species responsible for the electronic conductivity, essential for many applications of TiO₂, especially photocatalysis (Di Valentin et al., 2009). The surface Ti³⁺ species are unstable and can be quickly oxidized by oxygen in air or water, developing a method to synthesize black TiO₂ materials that with improved visible-light photocatalytic activity is a challenge (Zheng et al., 2013).

A FUNDAMENTAL PROCESS IN PHOTOCATALYTIC ACTIVITY OF BLACK TiO₂

In the past years, black titanium oxide has attracted attention in different fields, such as photocatalytic pollutants degradation (Chen et al., 2011; Li et al., 2019; Plodinec et al., 2019), photocatalytic hydrogen production through water splitting (Wang et al., 2017; Pan et al., 2019), photocatalytic CO₂ reduction (Qingli et al., 2015; Zhao et al., 2016; Gao et al., 2020), solar-thermal material (Ye et al., 2017), supercapacitor (Zhi et al., 2016; Huang et al., 2018), photoanode in Dye-Sensitized Solar Cells (Ullattil et al., 2017), Lithium-ion batteries (Kim et al., 2017) (Yang et al., 2018), and medicine (Ni et al., 2017; Mazare et al., 2019).

The principle of the semiconductors photocatalysis consists of the following components: photon absorption, carriers separation, carrier diffusion simultaneously with carrier transport, catalytic efficiency and mass transfer of reactants and products (Takanabe, 2017).

Photon absorption: if the semiconductor has energy equal to or greater than E_g and consequent excitation of electrons (e⁻) to the CB leaving positively charged vacancies, holes (h⁺), in the VB (**Figure 1**)

Carriers separation: the heterojunction between nanoparticles can better band gap arrangement, to improve the separation of photo-generated charge carriers (**Figure 1**), which is advantageous of improving the photocatalytic performance. The oxygen vacancy defects and Ti³⁺ centers on the surface of TiO₂ favor the separation of charge carriers (electrons and holes) and can trap the hole.

Carrier diffusion simultaneously with carrier transport. The photo-generated electrons can initiate the reduction processes, including O₂ reduction to superoxides, H₂ generation, and CO₂ reduction to methane, methanol, or formaldehyde

(Wen et al., 2015). The electron transfer is significant for the knowledge of the fundamental concepts of photocatalytic processes and to have an opinion about design and industrialization of the photocatalytic process (Mohamed and Bahnemann, 2012).

The transfer of electron/hole pairs to the interface initiates the redox reaction. The lifetime of the photo-generated charge carrier determines the efficiency of photocatalytic processes (Takanabe, 2017). Hence, increasing the efficiency of charge separation/transport in semiconductor nanoparticles is one of the major problems in photocatalysis to be addressed by the black TiO₂.

The presence of oxygen vacancies in TiO₂ can efficiently extend the visible light absorption range of titania because the localized oxygen vacancy states are located at 0.75 to 1.18 eV below the conduction band of TiO₂ (Asahi et al., 2001) (**Figure 1**). The hydroxyl radicals (HO•) can be formed when hydroxyl anions (HO⁻), and adsorbed water trap the holes, which are capable of degrading the organic pollutants in wastewater.

SUMMARY AND OUTLOOK

The current review focuses on the investigation of the chemical reduction synthetic route for black TiO₂ nanomaterials, and their applications related to the environmental application such as photodegradation of organic pollutants and photocatalytic water splitting.

Since 1972, when Fujishima and Honda (Fujishima and Honda, 1972) reported about the water-splitting process using a TiO₂ electrode under UV irradiation, photocatalysis has attracted attention. The solar-driven applications of TiO₂ have been limited due to its band-gap (around 3.2 eV). A remarkable step in solar-driven photocatalysis was presented in 2011 by Chen and co-authors when black TiO₂ enhanced the photocatalytic activity of TiO₂. In the last years, many studies have focused on the synthesis and explanation of different properties of black-TiO₂ to improve the activity of the photocatalyst under visible irradiation. An important drawback is the synthesis requirements such as long annealing treatments (a few days), and the high pressure of hydrogen atmosphere, up to 20 bar.

The colored TiO₂ can turn from white to yellow, blue, brown or black, due to the change in optical properties (modification of its band-gap), and defects in the surface layers that enhanced solar light adsorption and photocatalytic reactions. Among the colored forms, black TiO₂ has been one of the most investigated because it can get excellent optical, chemical and electronic properties due to at least one of these characteristics: the presence of Ti³⁺ ions, oxygen vacancies undetectable in white TiO₂ and usually present in black TiO₂, structural disorder/defects in the surface, Ti-OH groups, Ti-H groups, and modifications of the valence band edge. The colored TiO₂ has rich oxygen vacancies and Ti³⁺ defects, which conduct to better conductivity for electron transfer, increased visible absorption and higher conduction band

potential. The oxygen vacancies and Ti³⁺ defects can act as traps for reducing the recombination of e⁻/h⁺ pairs and enhancing the photocatalytic activity.

The chemical reduction methods include the reduction of TiO₂ with active hydrogen species such as H₂, H₂/Ar or H₂/N₂ gases, using high temperatures with active metals such as aluminum, magnesium and zinc powders, or the reduction of TiO₂ in solution with NaBH₄ and organic molecules such as imidazole and ascorbic acid can effectively lead to the color change of TiO₂ into black color. The color change of TiO₂ depends on the synthesis conditions, such as pressure, temperature, time, and the reducing agent, featuring different structural (lattice changes or disordering), chemical (formation of Ti³⁺, oxygen vacancies, Ti-H, Ti-OH), physical properties (such as optical properties), and photocatalytic activities in both hydrogen generation and organic pollutant removal. The thermal treatment changes the color of the samples between yellow at 300–350°C, brown at 400°C and black above 450°C, the crystal structure has no major changes due to hydrogenation.

REFERENCES

- Asahi, R., Morikawa, T., Ohwaki, T., Aoki, K., and Taga, Y. (2001). Visible-light photocatalysis in nitrogen-doped titanium oxides. *Science* 293, 269–271. doi: 10.1126/science.1061051
- Bi, X., Du, G., Sun, D., Zhang, M., Yu, Y., Su, Q., et al. (2020). Room-temperature synthesis of yellow TiO₂ nanoparticles with enhanced photocatalytic properties. *Appl. Surf. Sci.* 511:145617. doi: 10.1016/j.apsusc.2020.145617
- Chen, X., Liu, L., and Huang, F. (2015). Black titanium dioxide (TiO₂) nanomaterials. *Chem. Soc. Rev.* 44, 1861–1885 doi: 10.1039/C4CS00330F
- Chen, X., Liu, L., Yu, P. Y., and Mao, S. S. (2011). Increasing solar absorption for photocatalysis with black hydrogenated titanium dioxide nanocrystals. *Science* 331, 746–750. doi: 10.1126/science.1200448
- Cui, H., Zhao, W., Yang, C., Yin, H., Lin, T., Shan, Y., et al. (2014). Black TiO₂ nanotube arrays for high-efficiency photoelectrochemical water-splitting. *J. Mater. Chem. A* 2, 8612–8616. doi: 10.1039/C4TA00176A
- Di Valentin, C., Pacchioni, G., and Selloni, A. (2009). Reduced and n-type doped TiO₂: nature of Ti³⁺ species. *J. Phys. Chem. C* 113, 20543–20552. doi: 10.1021/jp9061797
- Fang, W., Xing, M., and Zhang, J. (2014). A new approach to prepare Ti³⁺ self-doped TiO₂ via NaBH₄ reduction and hydrochloric acid treatment. *Appl. Catal. B Environ.* 160–161, 240–246. doi: 10.1016/j.apcatb.2014.05.031
- Fujishima, A., and Honda, K. (1972). Electrochemical photolysis of water at a semiconductor electrode. *Nature* 238, 37–38. doi: 10.1038/238037a0
- Gao, J., Shen, Q., Guan, R., Xue, J., Liu, X., Jia, H., et al. (2020). Oxygen vacancy self-doped black TiO₂ nanotube arrays by aluminothermic reduction for photocatalytic CO₂ reduction under visible light illumination. *J. CO₂ Util.* 35, 205–215. doi: 10.1016/j.jcou.2019.09.016
- Haider, A. J., Jameel, Z. N., and Al-Hussaini, I. H. M. (2019). Review on: titanium dioxide applications. *Enrgy. Proced.* 157, 17–29. doi: 10.1016/j.egypro.2018.11.159
- Hamilton, J. W. J., Byrne, J. A., Dunlop, P. S. M., Dionysiou, D. D., Pelaez, M., O'Shea, K., et al. (2014). Evaluating the mechanism of visible light activity for N,F-TiO₂ using photoelectrochemistry. *J. Phys. Chem. C* 118, 12206–12215. doi: 10.1021/jp4120964
- Hu, Y. H. (2012). A highly efficient photocatalyst-hydrogenated black TiO₂ for the photocatalytic splitting of water. *Angew. Chem. Int. Ed.* 51, 12410–12412. doi: 10.1002/anie.201206375
- Huang, C. H., Meen, T. H., Ji, L. W., Chao, S. M., Wu, T. L., Tsai, J. K., et al. (2018). Effects of TiO₂ nanoparticle doping in coconut-shell carbon on the properties of supercapacitor. *Sens. Mater.* 30, 645–653. doi: 10.18494/SAM.2018.1769
- Isac, L., Cazan, C., Enesca, A., and Andronic, L. (2019). Copper sulfide based heterojunctions as photocatalysts for dyes photodegradation. *Front. Chem.* 7:694. doi: 10.3389/fchem.2019.00694
- Jayashree, S., and Ashokkumar, M. (2018). Switchable intrinsic defect chemistry of titania for catalytic applications. *Catalysts* 8, 1–26. doi: 10.3390/catal8120601
- Jedsukontorn, T., Ueno, T., Saito, N., and Hunsom, M. (2017). Facile preparation of defective black TiO₂ through the solution plasma process: effect of parametric changes for plasma discharge on its structural and optical properties. *J. Alloys Compd.* 726, 567–577. doi: 10.1016/j.jallcom.2017.08.028
- Kang, Q., Cao, J., Zhang, Y., Liu, L., Xu, H., and Ye, J. (2013). Reduced TiO₂ nanotube arrays for photoelectrochemical water splitting. *J. Mater. Chem. A* 1, 5766–5774. doi: 10.1039/c3ta10689f
- Kim, D. S., Chung, D. J., Bae, J., Jeong, G., and Kim, H. (2017). Surface engineering of graphite anode material with black TiO_{2-x} for fast chargeable lithium ion battery. *Electrochim. Acta* 258, 336–342. doi: 10.1016/j.electacta.2017.11.056
- Lee, K., Mazare, A., and Schmuki, P. (2014). One-dimensional titanium dioxide nanomaterials: nanotubes. *Chem. Rev.* 114, 9385–9454. doi: 10.1021/cr500061m
- Leshuk, T., Linley, S., and Gu, F. (2013). Hydrogenation processing of TiO₂ nanoparticles. *Can. J. Chem. Eng.* 91, 799–807. doi: 10.1002/cjce.21745
- Li, G., Lian, Z., Li, X., Xu, Y., Wang, W., Zhang, D., et al. (2015). Ionothermal synthesis of black Ti³⁺-doped single-crystal TiO₂ as an active photocatalyst for pollutant degradation and H₂ generation. *J. Mater. Chem. A* 3, 3748–3756. doi: 10.1039/C4TA02873B
- Li, Z., Bian, H., Xiao, X., Shen, J., Zhao, C., Lu, J., et al. (2019). Defective black TiO₂ nanotube arrays for enhanced photocatalytic and photoelectrochemical applications. *ACS Appl. Nano Mater.* 2, 7372–7378. doi: 10.1021/acsnm.9b01878
- Liu, L., Yu, P. Y., Chen, X., Mao, S. S., and Shen, D. Z. (2013). Hydrogenation and disorder in engineered black TiO₂. *Phys. Rev. Lett.* 111:065505. doi: 10.1103/PhysRevLett.111.065505
- Liu, Y., Tian, L., Tan, X., Li, X., and Chen, X. (2017). Synthesis, properties, and applications of black titanium dioxide nanomaterials. *Sci. Bull.* 62, 431–441. doi: 10.1016/j.scib.2017.01.034
- Mazare, A., Park, J., Simons, S., Mohajernia, S., Hwang, I., Yoo, J. E., et al. (2019). Black TiO₂ nanotubes: efficient electrodes for triggering electric field-induced stimulation of stem cell growth. *Acta Biomater.* 97, 681–688. doi: 10.1016/j.actbio.2019.08.021
- Mohamed, H. H., and Bahnmann, D. W. (2012). The role of electron transfer in photocatalysis: fact and fictions. *Appl. Catal. B* 128, 91–104. doi: 10.1016/j.apcatb.2012.05.045

AUTHOR CONTRIBUTIONS

LA planned the content and wrote the manuscript. AE contributed to the photocatalysis chapter. All authors contributed to the article and approved the submitted version.

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- Naldoni, A., Altomare, M., Zoppellaro, G., Liu, N., Kment, Š., Zboril, R., et al. (2019). Photocatalysis with reduced TiO₂: from black TiO₂ to cocatalyst-free hydrogen production. *ACS Catal.* 9, 345–364. doi: 10.1021/acscatal.8b04068
- Ni, W., Li, M., Cui, J., Xing, Z., Li, Z., Wu, X., et al. (2017). 808 nm light triggered black TiO₂ nanoparticles for killing of bladder cancer cells. *Mater. Sci. Eng. C* 81, 252–260. doi: 10.1016/j.msec.2017.08.020
- Ou, G., Xu, Y., Wen, B., Lin, R., Ge, B., Tang, Y., et al. (2018). Tuning defects in oxides at room temperature by lithium reduction. *Nat. Commun.* 9:1302. doi: 10.1038/s41467-018-03765-0
- Pan, J., Dong, Z., Wang, B., Jiang, Z., Zhao, C., Wang, J., et al. (2019). The enhancement of photocatalytic hydrogen production via Ti³⁺ self-doping black TiO₂/g-C₃N₄ hollow core-shell nano-heterojunction. *Appl. Catal. B* 242, 92–99. doi: 10.1016/j.apcatb.2018.09.079
- Plodinec, M., Grčić, I., Willinger, M. G., Hammud, A., Huang, X., Panžić, I., et al. (2019). Black TiO₂ nanotube arrays decorated with Ag nanoparticles for enhanced visible-light photocatalytic oxidation of salicylic acid. *J. Alloys Compd.* 776, 883–896. doi: 10.1016/j.jallcom.2018.10.248
- Qingli, W., Zhaoguo, Z., Xudong, C., Zhengfeng, H., Peimei, D., Yi, C., et al. (2015). Photoreduction of CO₂ using black TiO₂ films under solar light. *J. CO₂ Util.* 12, 7–11. doi: 10.1016/j.jcou.2015.09.001
- Rajaraman, T. S., Parikh, S. P., and Gandhi, V. G. (2020). Black TiO₂: a review of its properties and conflicting trends. *Chem. Eng. J.* 389:123918. doi: 10.1016/j.cej.2019.123918
- Ren, R., Wen, Z., Cui, S., Hou, Y., Guo, X., and Chen, J. (2015). Controllable synthesis and tunable photocatalytic properties of Ti³⁺-doped TiO₂. *Sci. Rep.* 5:10714. doi: 10.1038/srep10714
- Schlesinger, H. I., Brown, H. C., Finholt, A. E., Gilbreath, J. R., Hoekstra, H. R., and Hyde, E. K. (1953). Sodium borohydride, its hydrolysis and its use as a reducing agent and in the generation of hydrogen. *J. Am. Chem. Soc.* 75, 215–219. doi: 10.1021/ja01097a057
- Seok, D., Il, W. u, M., Shim, K. B., Kang, Y., and Jung, H. K. (2016). High-rate performance of Ti³⁺ self-doped TiO₂ prepared by imidazole reduction for Li-ion batteries. *Nanotechnology* 27, 1–5. doi: 10.1088/0957-4484/27/1/43/435401
- Sinhmahapatra, A., Jeon, J. P., and Yu, J. S. (2015). A new approach to prepare highly active and stable black titania for visible light-assisted hydrogen production. *Energy Environ. Sci.* 8, 3539–3544. doi: 10.1039/C5EE02443A
- Song, H., Li, C., Lou, Z., Ye, Z., and Zhu, L. (2017). Effective formation of oxygen vacancies in black TiO₂ nanostructures with efficient solar-driven water splitting. *ACS Sustain. Chem. Eng.* 5, 8982–8987. doi: 10.1021/acssuschemeng.7b01774
- Su, J., Zou, X., and Chen, J. S. (2014). Self-modification of titanium dioxide materials by Ti³⁺ and/or oxygen vacancies: new insights into defect chemistry of metal oxides. *RSC Adv.* 4, 13979–13988. doi: 10.1039/C3RA47757F
- Takanabe, K. (2017). Photocatalytic water splitting: quantitative approaches toward photocatalyst by design. *ACS Catal.* 7, 8006–8022. doi: 10.1021/acscatal.7b02662
- Tan, H., Zhao, Z., Niu, M., Mao, C., Cao, D., Cheng, D., et al. (2014). A facile and versatile method for preparation of colored TiO₂ with enhanced solar-driven photocatalytic activity. *Nanoscale* 6, 10216–10223. doi: 10.1039/C4NR02677B
- Tian, M., Mahjouri-Samani, M., Eres, G., Sachan, R., Yoon, M., Chisholm, M. F., et al. (2015). Structure and formation mechanism of black TiO₂ nanoparticles. *ACS Nano* 9, 10482–10488. doi: 10.1021/acsnano.5b04712
- Ullattil, S. G., Narendranath, S. B., Pillai, S. C., and Periyat, P. (2018). Black TiO₂ nanomaterials: a review of recent advances. *Chem. Eng. J.* 343, 708–736. doi: 10.1016/j.cej.2018.01.069
- Ullattil, S. G., Thelappurath, A. V., Tadka, S. N., Kavil, J., Vijayan, B. K., and Periyat, P. (2017). A sol-solvent thermal processed 'Black TiO₂' as photoanode material in dye sensitized solar cells. *Sol. Energy* 155, 490–495. doi: 10.1016/j.solener.2017.06.059
- Wajid Shah, M., Zhu, Y., Fan, X., Zhao, J., Li, Y., Asim, S., et al. (2015). Facile synthesis of defective TiO_{2-x} nanocrystals with high surface area and tailoring bandgap for visible-light photocatalysis. *Sci. Rep.* 5:15804. doi: 10.1038/srep15804
- Wang, B., Shen, S., and Mao, S. S. (2017). Black TiO₂ for solar hydrogen conversion. *J. Materiomics* 3, 96–111. doi: 10.1016/j.jmat.2017.02.001
- Wang, C. C., and Chou, P. H. (2016). Effects of various hydrogenated treatments on formation and photocatalytic activity of black TiO₂ nanowire arrays. *Nanotechnology* 27, 1–9. doi: 10.1088/0957-4484/27/32/325401
- Wang, Z., Yang, C., Lin, T., Yin, H., Chen, P., Wan, D., et al. (2013). Visible-light photocatalytic, solar thermal and photoelectrochemical properties of aluminium-reduced black titania. *Energy Environ. Sci.* 6, 3007–3014. doi: 10.1039/c3ee41817k
- Wen, J., Li, X., Liu, W., Fang, Y., Xie, J., and Xu, Y. (2015). Photocatalysis fundamentals and surface modification of TiO₂ nanomaterials. *Chinese J. Catal.* 36, 2049–2070. doi: 10.1016/S1872-2067(15)60999-8
- Xin, X., Xu, T., Yin, J., Wang, L., and Wang, C. (2015). Management on the location and concentration of Ti³⁺ in anatase TiO₂ for defects-induced visible-light photocatalysis. *Appl. Catal. B* 176–177, 354–362. doi: 10.1016/j.apcatb.2015.04.016
- Xu, J., Zhang, J., Cai, Z., Huang, H., Huang, T., Wang, P., et al. (2019). Facile and large-scale synthesis of defective black TiO_{2-x} (B) nanosheets for efficient visible-light-driven photocatalytic hydrogen evolution. *Catalysts* 9, 2–9. doi: 10.3390/catal9121048
- Yan, X., Li, Y., and Xia, T. (2017). Black titanium dioxide nanomaterials in photocatalysis. *Int. J. Photoenergy* 2017:8529851. doi: 10.1155/2017/8529851
- Yang, Y., Shi, W., Liao, S., Zhang, R., and Leng, S. (2018). Black defect-engineered TiO₂ nanocrystals fabricated through square-wave alternating voltage as high-performance anode materials for lithium-ion batteries. *J. Alloys Compd.* 746, 619–625. doi: 10.1016/j.jallcom.2018.02.309
- Ye, M., Jia, J., Wu, Z., Qian, C., Chen, R., O'Brien, P. G., et al. (2017). Synthesis of black TiO_x nanoparticles by Mg reduction of TiO₂ nanocrystals and their application for solar water evaporation. *Adv. Energy Mater.* 7:1601811. doi: 10.1002/aenm.201601811
- Zhang, K., and Park, J. H. (2017). Surface localisation of defects in black TiO₂: enhancing photoactivity or reactivity. *J. Phys. Chem. Lett.* 8, 199–207. doi: 10.1021/acs.jpcc.6b02289
- Zhao, J., Li, Y., Zhu, Y., Wang, Y., and Wang, C. (2016). Enhanced CO₂ photoreduction activity of black TiO₂-coated Cu nanoparticles under visible light irradiation: role of metallic Cu. *Appl. Catal. A Gen.* 510, 34–41. doi: 10.1016/j.apcata.2015.11.001
- Zheng, Z., Huang, B., Meng, X., Wang, J., Wang, S., Lou, Z., et al. (2013). Metallic zinc-assisted synthesis of Ti³⁺ self-doped TiO₂ with tunable phase composition and visible-light photocatalytic activity. *Chem. Commun.* 49, 868–870. doi: 10.1039/C2CC37976G
- Zhi, J., Yang, C., Lin, T., Cui, H., Wang, Z., Zhang, H., et al. (2016). Flexible all solid state supercapacitor with high energy density employing black titania nanoparticles as a conductive agent. *Nanoscale* 8, 4054–4062. doi: 10.1039/C5NR08136J
- Zhu, G., Shan, Y., Lin, T., Zhao, W., Xu, J., Tian, Z., et al. (2016). Hydrogenated blue titania with high solar absorption and greatly improved photocatalysis. *Nanoscale* 8, 4705–4712. doi: 10.1039/C5NR07953E
- Zu, D., Wang, H., Lin, S., Ou, G., Wei, H., Sun, S., et al. (2019). Oxygen-deficient metal oxides: synthesis routes and applications in energy and environment. *Nano Res.* 12, 2150–2163. doi: 10.1007/s12274-019-2377-9

Conflict of Interest: The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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