Black TiO₂ Nanomaterials: A Review of Recent Advances

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Abstract

Recently reported black TiO₂ nanomaterials are the unequivocally accepted sun light harvesters which facilitate the maximum solar energy absorption from ultraviolet (UV) to infrared (IR) region of the solar spectrum due to their improved optical absorption properties in comparison to the normal white TiO₂. The recent advancement in black TiO₂ nanomaterials explicitly proved that the structural and morphological features along with the suitable electronic properties are being extensively utilized in many areas of research. The current review focuses on the various synthetic routes for black TiO₂ nanomaterials, their structure, morphological variations, electronic structure and their diverse applications related to environmental and technological fields such as photocatalysis, solar photocatalytic water splitting, dye sensitized solar cells, batteries, supercapacitors and photothermal therapy.

1. Introduction

The maximum utilization of renewable energy resources such as sun light, wind, biomass, rain, tides and waves are required to address the energy demand of 21st century [1,2]. Among these renewable sources, solar energy is quite important because sun is the ubiquitous energy source and solar energy is available abundantly with free of cost [3,4]. Diverse pathways that could easily harvest the sunlight to encounter the future energy demands generated significant interest among the scientific community [5,6]. Harnessing the abundant sunlight falling on earth has been a constant challenge to mankind. In this scenario, nanomaterial architectures for solar energy conversion play an important role in harvesting the sunlight. Materials with smaller particle size inhibits the recombination probability of photogenerated electrons and
holes on its surface thereby facilitating their smooth transport. In addition, nanoparticles possess high surface area which contains more active sites on the surface [6]. Among the various nanomaterials reported so far, TiO2 is the most promising light harvesting material that has been widely investigated [1–10]. The light harvesting potential of white TiO2 has been experimentally manifested in the fields of photo-degradation [7–10], dye sensitized solar cells [11–14], self-cleaning coatings [15–19], solar water splitting [20–25], organic reactions [26–29], photocatalytic sensors [30–35] etc. TiO2 has been widely accepted as a light harvester because of its chemical and thermal stability, high refractive index, nontoxicity, and wide band gap energy [36–42]. A good portion of the sun’s radiation is in the visible (43%) and infra red (52%) range with 5% in ultra violet region [43]. A colorless/white material can only absorb energy from the UV region. Pure TiO2 is a colorless white crystalline solid which absorbs in the UV region only [44], researchers have imposed doping on TiO2 for the improvement of its wavelength absorption from UV to visible region [1–10]. Metal doping in TiO2 nanomaterials generated secondary impurities (e.g. Al2TiO5, CeTiO2, and Ce2TiO3). Presence of these impurity phases decreased the crystallinity of TiO2 which in turn reduced the efficiency [45] and photocatalytic activity of the material [1–46]. Non-metal doping has also been investigated widely for better light absorption. The light harvesting process using non-metal doped TiO2 has been successfully implemented without developing any impurity phases after the annealing process [47–50]. However, non-metal doped TiO2 structures were incapable of absorbing IR region which covers 52% of the solar spectrum [1–51]. In order to harvest sunlight more effectively blue [52–60], yellow [61,62], brown [63,64] red [65–67] and grey [68–70] TiO2 have also been reported. However, they all possessed limited or even zero absorption in the IR region of the solar spectrum.

In 1950’s Czromzeyer and Gilleo compared the optical absorption characteristics of bare and hydrogenated rutile single crystals [71]. The hydrogenated rutile become blue in color by extending its absorption from visible to IR region of the electromagnetic spectra. Afterwards extensive works had been carried out to utilize the wide optical absorption features of TiO2 which led to the developments of black TiO2, an ultimate solar light absorber [72–76]. Black TiO2 is first produced when white TiO2 was heated at 200°C under 20.0 bar hydrogen pressure for 5 days by Chen et al. in 2011 [77]. After this discovery of black TiO2 nanoparticlea, the synthesis of black TiO2 nanostructures for energy applications is found to be a hot area in the current environmental perspective [78]. The current review addresses the latest developments in black TiO2 nanomaterials. Various synthetic aspects of black TiO2 nanomaterials and characterization techniques to probe its structural, morphological and optical properties were surveyed. The theoretical basis of color change in black TiO2 nanomaterials and its correlation with the optical absorption features were discussed in detail. This review gave great emphasis on various functional applications of black TiO2 nanomaterials [77–192].

1.1. What is black TiO2?

Pure TiO2 has a white color with a band gap of 3.0–3.2 eV [79]. The wide band gap in TiO2 inhibits the proper utilization of entire solar spectrum. Diverse methodologies have been tested for improving the optical and electronic properties of TiO2, viz, dopin [80], dye sensitization [80], metal organic frame works [81], TiO2 composites [82] etc. All these strategies could red shift the absorption edge of TiO2, but these modifications on TiO2 could not harvest the entire solar energy falling on earth. White TiO2 turns black on reduction through various methods. Presence of Ti3+ through self-doping, surface hydroxyl groups, oxygen vacancies and Ti-H bonds in black TiO2 consequent to the structural modifications were responsible for the black coloration as well as the superior optical, electronic and catalytic properties [83]. As shown in Fig. 1, black TiO2 nanomaterial has the potential to absorb the entire range of solar spectra.

Lattice disorder is introduced in the formation of black TiO2 which has resulted in the creation of mid gap energy levels within the band gap. The wide range of absorption in these nanoparticles consequent to this mid-gap energy levels distribution is the key factor for the optical and catalytic activity.

2. Synthesis of black TiO2 nanostructures

Different strategies have been employed for the synthesis of black TiO2 nanomaterial towards various functional applications [77–192]. To date, hydrogenation is the widely used method for synthesizing black TiO2. High/low pressure hydrogen treatment, hydrogen-argon treatment, hydrogen-nitrogen treatment, argon treatment, hydrogen plasma treatment, electrochemical reduction, chemical oxidation/reduction, hydroxylation and pulsed laser ablation are the main synthetic methods carried out so far. Even though Hydrogenation has been the most employed method for synthesizing black TiO2, all those hydrogenation procedures were not ended in black TiO2 [68,69].

2.1. High/low pressure hydrogen treatment

Synthesis of black TiO2 was first reported by Chen et al. using hydrogenation of crystalline TiO2 at a high pressure of 20 bar [77]. The synthesized white TiO2 nanocrystals were hydrogenated in a 20 bar H2 atmosphere at 200°C for 5 days [77]. The reduction in effective band gap was (Fig. 2A) due to the disordered layer on the surface of black TiO2 induced by hydrogenation, which was beneficial for carrier trapping. The extended disorder present in the nanocrystal creates mid-gap states, instead of discrete donor levels, which will effectively overlap with the conduction band edge. The crystalline state of pristine TiO2 and the disordered surface of black TiO2 (Fig. 2B) were also visible from HRTEM images (Fig. 2C and D) [77].

Sun et al. reported the hydrogen incorporation into anatase TiO2 nanocrystals under high hydrogen pressure and they obtained hydrogenated black TiO2-(1 0 1) [84]. They synthesized anatase TiO2 nanocrystals predominantly having (0 0 1) and (1 0 1) separately. Hydrogen adsorption and desorption properties were analyzed by an automated Sieverts’s apparatus. TiO2 with (1 0 1) and (0 0 1) surfaces have a hydrogen storage capacity of 1.4% and 1.0% respectively as represented in Fig. 3. Computational calculations based on DFT theory showed that hydrogen occupied the voids created by adjacent titanium-oxygen octahedra and hydrogen incorporation through the anatase (1 0 1) surface.
is favorable than that of (0 0 1) (Fig. 4) [84].

Leshuk et al. reported hydrogenation of pristine TiO$_2$ nanoparticles at different temperatures. The color change and a large wavelength absorption was observed for sample hydrogenated at 450 °C under 20 bar pressure for 24 h [85]. The color change observed and the corresponding absorption change (Tauc Plot) are shown in Fig. 5.

All the above methods were carried out at elevated temperatures ranges from 200 to 450 °C under high hydrogen pressure of 20 bar. However, Lu et al. experimented to synthesize black TiO$_2$ nanoparticles at ambient temperature under high-pressure H$_2$ treatment on commercial P25 and examined the color change of these TiO$_2$ nanoparticles over time (0–20 days) [86]. The color of commercial P25 turned to black after 20 days of hydrogenation (Fig. 6). The optical absorption onset of this black TiO$_2$ nanoparticle was about 1.0 eV lower compared to P25 [86].

Wang et al. reported the synthesis of black TiO$_2$ by hydrogenation of rutile TiO$_2$ nanowire arrays under ultrahigh pure hydrogen atmosphere for 3 h at 200–550 °C [87]. The color of the hydrogenated rutile TiO$_2$ nanowires turned to yellowish green at 350 °C and black at 450 °C. This hydrogenated rutile TiO$_2$ nanowires had visible light absorption because of hydrogen treatment [87].

Naldoni et al. attempted to synthesize black TiO$_2$ nanoparticles by heating amorphous TiO$_2$ under H$_2$ flow, followed by rapid cooling in an inert environment [88]. Here they pretreated TiO$_2$ powder under
vacuum followed by heat treatment at 200 °C for 1 h under O₂ atmosphere and subsequent reduction at 500 °C for 1 h in hydrogen atmosphere. The amorphous precursor is more viable for black TiO₂ with large wavelength absorption compared to that of the crystalline precursors such as P25 [88]. In a similar method, Zhang et al. employed hydrogenation to obtain the mesoporous black TiO₂ nanosheets by using a biotemplate (Typha angustifolia). This scheme is represented in Fig. 7 [89]. Liu et al. reported the synthesis of black TiO₂ nanomaterials using anatase TiO₂ nanotubes as precursor [90].

2.2. Hydrogen-Argon treatment

Another method of synthesis of black TiO₂ was using Hydrogen-Argon treatment. Leshuk et al. compared the color change of TiO₂ nanoparticles obtained after reduction under pure H₂ and H₂-Ar mixture. They inferred that the color change depended upon the preparation methods of precursors [91]. Various anatase nanomorphologies were hydrogenated by Lu et al. under H₂-Ar mixture at 450 °C for 1 h [92]. Sinhamahapatra et al. developed a controlled magnesiothermal reduction to synthesize reduced black TiO₂ under H₂/Ar atmosphere [93]. The material possessed remarkable improved progress in the visible and infrared absorption features. Here the commercially available nano anatase TiO₂ was treated under different concentration of Mg followed by 5% H₂/Ar treatment to obtain black TiO₂ [93].

2.3. Argon-Nitrogen treatment

TiO₂-B (TiO₂-B structure is comprised of edge- and corner-shared TiO₆ octahedra. In fact, TiO₂-B could be seen as distorted octahedra structure) nanoparticles were also converted into black TiO₂ in an Ar-N₂ environment [94]. The monodispersed TiO₂-B particles obtained by the hydrolysis of TiCl₄ in ethylene glycol were suspended in methanol (20 mL) and then subjected to irradiation under UV light in a sealed container with constant bubbling of N₂, turning the solution black in color. The black TiO₂-B nanoparticles were obtained by heating the solid product obtained in the above process at 340 °C in Ar atmosphere for 2 h [94]. Wei et al. reported a core-shell black anatase TiO₂ with a
high concentration of Ti$^{3+}$ and oxygen vacancy defects by a one-pot synthetic method viz. calcination of colloidal TiO$_2$ precursor under N$_2$ atmosphere alone. (Fig. 8) [95].

2.4. Hydrogen-Nitrogen treatment

Zhu et al. manipulated black TiO$_2$ through hydrogen spill in a H$_2$-N$_2$ atmosphere at 200–700 °C [96]. They hydrogenated platinum impregnated P25 (Pt-P25) under H$_2$-N$_2$ mixture. It could be observed that the reduction started from 160 °C. Further increase in temperature up to 750 °C causes a color change into black due to the hydrogen spillover from Pt to TiO$_2$. Wu et al. prepared black TiO$_2$ nanoparticles by combining the sol-gel strategy and H$_2$-N$_2$ treatment. Sol-gel derived nanocrystalline TiO$_2$ was treated under H$_2$:N$_2$ environment to obtain black TiO$_2$ [97]. Thermal treatment at different temperatures (110, 130, 150, 170, 190 and 210 °C) on protonated titanate nanotubes under H$_2$:N$_2$ atmosphere resulted to a series of nanotubes and nanobelts [98]. The nanotube morphology was retained at temperature ≤150 °C and above that temperature, the morphology was changed to nanobelts along with the phase change from anatase to TiO$_2$-B [98].

2.5. Argon treatment

Zhang et al. reported Ar treatment of sol-gel derived Ni doped TiO$_2$ leading to the formation of black TiO$_2$ nanoparticles [99]. The black TiO$_2$ precursor (Ni doped TiO$_2$) was mixed with 2 g of NaBH$_4$ and heated at 350 °C under Ar atmosphere for 1 h. Finally allowed to cool naturally until it reaches room temperature. The color of the Ni doped TiO$_2$ nanoparticles was yellowish. The various samples such as 0, 1.0, 2.0, 3.0, and 4.0 mol% of Ni were denoted as M0, M1, M2, M3, and M4 respectively. These materials are turned from yellowish to black when treated under Ar atmosphere and were denoted as b-M0, b-M1, b-M2, bM3, and b-M4, respectively. The change in color and absorbance spectra along with the Tauc plot before and after 2 mol% Ni doping and Ar treatment are shown in Fig. 9 [99]. Grabstanowicz et al. prepared black TiO$_2$ powders using a two-step strategy [100]. The Ti precursor
used was TiH2 and it was mixed with H2O2 to get a slurry. Further the slurry turned yellow on vacuum dessication and drying at 100 °C and finally the yellow powder was heated at 630 °C for 3 h in Ar atmosphere to obtain the black rutile TiO2 possessed markedly increased absorption in the visible and near-infrared regions [100]. Myung et al. reported hydrogenation under Ar treatment for the synthesis of black TiO2 by annealing a yellow TiO2 gel at 400–600 °C for 5 h [101].

2.6. Plasma treatment

Wang et al. prepared hydrogenated black TiO2 nanoparticles by hydrogen plasma in a thermal plasma furnace using 200 W plasma input power on commercial P25 sample [102]. This hydrogenated black TiO2 nanoparticles had a notable absorption characteristics in the visible and near infrared region (Fig. 10) [102].

Teng et al. manipulated black TiO2 nanotubes by hydrogen plasma assisted chemical vapor deposition with hydrogen as reaction gas [103]. Precursor TiO2 was subjected to heat at 350–500 °C for 3 h under the hot filament (2000 °C) resulted in black colored TiO2 nanotubes [103]. This method was also used by Yan et al. [104] where the processing was carried out at 390 °C for 3 h with the inductively coupled plasma power with H2 flow. The black TiO2 nanoparticles obtained had enhanced visible light absorption characteristics [104]. The same group have also employed H2 plasma treatment on Degussa-P25 drop
Initially the electrode surface got oxidized by the OH⁻ which were subjected to high frequency bipolar high voltage pulses plasma generated inside water between two metallic Ti electrodes, which were subjected to high frequency bipolar high voltage pulses plasma generated inside water between two metallic Ti electrodes. The process was considered as a green route to black TiO₂ [106]. Black TiO₂ nanoparticles were also reported by applying microwave induced plasma over a water soluble titanium complex (NH₄)₆[Ti₄(C₂H₂O₃)₄(C₂H₃O₃)₂(O₂)₄O₂].4H₂O [107].

2.7. NaBH₄ reduction

Kang et al. implemented a chemical reduction for the synthesis of black TiO₂ using NaBH₄ [108]. The reduction of TiO₂ nanotube had been carried out with 0.1 M NaBH₄ solution at room temperature for an hour. The reduced black TiO₂ nanotubes had strong absorption extending up to near-infrared [108]. Tan et al. employed a solid state synthesis route for black TiO₂. P₂5 (Anatase and Rutile) was ground thoroughly with NaBH₄ and the mixture was heated in a tubular furnace under Ar atmosphere at 300–400 °C for different time intervals up to 1 h. While cooling to room temperature different colored TiO₂ core-shell nanoparticles were obtained (Fig. 11) [109].

2.8. Metal reduction

Black TiO₂ nanoparticles could be synthesized through reduction with various metals. Aluminum, zinc and magnesium are identified as reducing agents to obtain black TiO₂. Wang et al. used Al as a reducing agent in an evacuated two-zone vacuum furnace at 300–500 °C [110]. The driving force behind the formation of black TiO₂ is the release of oxygen from pre-annealed TiO₂ to molten aluminum so that oxygen vacancies are created on TiO₂. In a typical procedure, pre-annealing of aluminum was done at 800 °C for 6 h and that of pristine TiO₂ was done at 500 °C for 20 h respectively. Further the post annealing was carried out at 800 and 900 °C for 12 h respectively. These reduced TiO₂ nanoparticles had black color and traversed absorption through visible-light to near-infrared regions (Fig. 12).

Cui et al. prepared black anatase TiO₂ nanotubes by a similar method in which they used an anodized Ti foil as precursor for Ti [111]. Ti foil was anodized in a mixture of ethylene glycol, 0.4 wt% NH₄F and 3 wt% H₂O under 100 V for 5 min. resulting in TiO₂ nanotubes. The first layer was removed followed by calcination at 500 °C for 4 h in air. The synthesized TiO₂ nanotubes and aluminum powders were heated at 500 and 850 °C in such a way that TiO₂ releases oxygen to molten aluminum to get reduced black TiO₂. The black anatase TiO₂ nanotubes had extended absorption from visible-light to near infrared regions [111].

Zhi et al. proposed another method for the synthesis of black TiO₂ where the white TiO₂ and aluminum metal were placed separately in a two-zone tube furnace and then evacuated to a base pressure lower than 0.5 Pa where TiO₂ and aluminum were heated for 6 h at 500 and 800 °C respectively under NH₃ atmosphere. After cooling to room temperature, black TiO₂ powders were formed [112]. Lin et al. synthesized a set of nonmetal-doped black TiO₂ with a more or less similar two-step strategy [113]. Here Al reduction was first carried out to introduce oxygen vacancies on the amorphous surface layer over the crystalline core of TiO₂ (Degussa P25) and then nonmetal elements such as H, N, S and I were introduced into the oxygen-deficient amorphous layers of Al-reduced TiO₂ nanocrystals (TiO₂-x) paved the way to color change. All these non-metal doped black TiO₂ nanoparticles have shown large wavelength absorption extended up to near-infrared region (Fig. 13) [113].

2.9. ZnCl₂/KCl molten salt assisted synthesis

In this method black TiO₂ hexagonal nanosheets were manipulated by mixing TiH₂ with a eutectic composition of ZnCl₂/KCl melt followed by grinding with ethanol for homogenization [114]. The homogenized powder was heated at 400 °C for 3 h. The product was cooled and dried to get black TiO₂. When the calcination temperature changes from 400, 450 to 500 °C, the morphology was changed from nanosheets, nanotubes and finally to nanorods [114].

2.10. Microwave assisted manganese reduction

Oxygen rich yellow anatase with visible light absorption and oxygen vacancy rich black anatase TiO₂ with NIR absorption have been synthesized [115]. In this method a sol has been synthesized using titanium butoxide, manganese acetate and water as precursors. Doping and hydroxylation were carried out simultaneously during the sol preparation and the sol was then put through microwave irradiation at 150 °C with stirring speed of 1200 rpm for 5 min followed by drying at 80 °C to obtain black anatase TiO₂ nanomaterials (Fig. 14).

2.11. Solvothermal synthesis

Shah et al. employed ascorbic acid as both reductant and structure directing agent to synthesis black TiO₂ [116]. Here different amounts of aqueous solution of L-ascorbic acid added to TiCl₃ and the pH was maintained to be 4 by adding NaOH solution. The mixture was heated at 180 °C for 12 h in an autoclave [116]. A one step solvothermal method for the synthesis of black TiO₂ on Ti foils with visible light absorption to near-infrared regions was reported by applying microwave induced plasma over a water soluble titanium complex (NH₄)₆[Ti₄(C₂H₂O₃)₄(C₂H₃O₃)₂(O₂)₄O₂].4H₂O [107].
absorption was also reported recently [117]. In the experiment, a piece of Ti foil was immersed in a mixture of aqueous NaOH and ethylene glycol in an autoclave and heated at 220 °C for 24 h. The product obtained was a black film of Na₂Ti₂O₄(OH). HCl solution was used to replace any Na⁺ with H⁺. Further annealing at 500 °C yielded black TiO₂ [117].

2.12. Ionothermal method

Single crystalline black Ti³⁺ doped TiO₂ was prepared using ionothermal method by Li et al. for efficient photocatalysis under solar illumination [118]. A buffer solution was made using Lithium acetate dihydrate along with glacial acetic acid and it was mixed in DMF solvent. A piece of cleaned Ti foil in an ionic liquid was placed in an autoclave along with the buffer solution in DMF. The autoclave was heated at 200 °C for 24 h and washed with ethanol followed by drying at 80 °C for 12 h [118].

2.13. Electrochemical Reduction-anodization

A two-step electrochemical reduction process (anodization technique) was performed by Xu et al. for the preparation of black TiO₂ nanotubes [119]. The anodization was carried out at 150 V for 1 h in ethylene glycol electrolyte containing 0.3 wt% NH₄F and 10 vol% H₂O₂ with a carbon rod as cathode and Ti as anode. TiO₂ nanotubes formed in the first was removed and subjected to second anodization and subsequent heating at 150 and 450 °C for 3 and 5 h respectively. The electrochemical reductive doping process was performed at room temperature under 5 V for 5–40 s in 0.5 M Na₂SO₄ aqueous solution where nanotubes as cathode and a Pt electrode as anode to obtain the black TiO₂ nanotube.

Zhang et al. implemented the similar strategy for fabricating black TiO₂ nanotubes [120]. The strategy is given in Fig. 15. Similarly, Li et al. also achieved black TiO₂ nanomaterials by the electrolytic reduction of TiO₂ nanotubes prepared by the anodization of Ti foil [121]. Zhou and Zhang synthesized black TiO₂ nanotubes with highly ordered nanotube arrays and appreciable optical absorbance [122]. A multipulse anodization strategy was introduced by Zheng et al. for the synthesis of black TiO₂ films [123].

Chen et al. implemented hydrothermal treatment on anodic TiO₂ nanotubes in deionised water, HCl and in NH₄OH [124]. The dissolution-precipitation of TiO₆²⁻ octahedra paved the way to crystalline anatase TiO₂ from the amorphous TiO₂ (Fig. 16). The polymorphs of TiO₂ (anatase, rutile and brookite) are composed of TiO₆²⁻ octahedra, and they differ only in their shared corners and edges. During the hydrothermal treatment a hydrated octahedral complex was formed on the surface of amorphous TiO₂ which contained Ti-OH and Ti-OH₂⁺ groups. The neighboring Ti-OH and Ti-OH₂⁺ groups underwent condensation through olation–oxolation processes to create Ti-O-Ti bridges which are the backbones of all TiO₂ structures. Anatase structure...
formation is energetically more favorable than that of other TiO$_2$ frameworks [124].

Dong et al. prepared black TiO$_2$ nanotubes by anodization followed by annealing [125]. The anodized Ti foil washed with ethanol and distilled water, dried at 150 °C and sintered at 450 °C for 1 h in ambient atmosphere. After removing the top oxide layer, a layer of black TiO$_2$ was obtained on the substrate [125].

2.14. Hydroxylation followed by ultrasonication

Recently Fan et al. observed the formation of black TiO$_2$ through prolonged ultrasonication [126]. They started with the simple procedure of making TiO$_2$ sol followed by ultrasonication for several hours and drying at 80 °C. It was also noted that with long duration of ultrasonication, the intensity of black color increases.

2.15. Pulsed laser ablation

A pulsed laser ablation technique was implemented by Chen et al. for the synthesis of black TiO$_2$ [127]. In this method an aqueous suspension of TiO$_2$ was taken into a cuvette. Nd:YAG pulsed laser was then used to irradiate TiO$_2$ inside the cuvette for different time intervals. The sample after 120 min irradiation was found to be black [127,128]. Pulsed laser irradiation on pristine TiO$_2$ led to oxygen release (oxygen vacancy production) leading to the formation of black TiO$_2-x$ was also reported recently [129].

2.16. Si quantum dot (QD) assisted chemical etching

Mesoporous black TiO$_2$ were prepared by Si QD assisted chemical etching [130]. The hydrogen terminated Si QD, were electrodeposited at the surface of Ti foil followed by chemical etching with HF. The H terminated Si QD facilitate the formation of Ti$_3^{3+}$ states and mesoporous black TiO$_2$ structure were formed [130].

2.17. Self doping via gel combustion

A one pot gel combustion strategy has been developed recently by our group (Fig. 17) [131]. A gel formed out of Titanium butoxide, diethylene glycol and water was heated at 300 °C for 2 h. Subsequently cooled rapidly. This aqueous mediated process led to the formation of anatase crystal phase at relatively low calcination temperatures [131].
in TiO2 nanoparticles were observed in many cases in which the mod-
s sense one can think of the band structure modi-
r ification of black TiO2 nanomaterials so far. Moreover, it explains the phase pro-
duction during the synthesis, morphology, structural, optical and ele-
tronic properties of TiO2. Finally application of the as synthesized black 
TiO2 were also shown in the Table 1.

3. Color transition and structural stability

In general the color of the white TiO2 materials are transformed into 
black. The extent of the transformation is determined by various factors 
such as extent of hydrogenation, extend of hydroxylation, doping, 
various synthesis parameters such as amount of reductants (g. Al, Zn, 
NaBH4, Ar, N2) used, reduction temperature, duration of reaction etc 
TiO2 nanoparticle s were observed in many cases in which the mod-
ifications affected the electronic structure [44,147–149]. Nitrogen 
doping in pristine TiO2 results in a yellow coloration due to the slight 
reduction of band gap [150]. The valence band edge of N doped TiO2 is 
shifted upwards due to the creation of new valence band levels as a 
result of intermixing of 2p orbitals of nitrogen and oxygen. In a similar 
se nce one can think of the band structure modification of black TiO2 
after hydrogen doping where the mid gap band states can be tailored by 
hydrogenation [151,154]. Here intermixing of orbitals of hydrogen and 
oxygen is not energetically favorable compared to the case of nitrogen and 
oxygen. So the extreme coloration of black TiO2 in view of the 
extended absorption towards IR region of electromagnetic spectra were 
studied in different aspects such as oxygen vacancy, presence of Ti3+ 
etc [152,153]. Pristine TiO2 has a fixed band gap which is constituted 
from valence band composed of O 2p orbitals and conduction bands 
formed by the Ti 3d orbitals. The enhanced optical absorption features 
of black TiO2 can be due to the formation and distribution of additional 
midgap energy levels or donor levels as a result there is an effective 
decrease in the band gap energy [77].

In the initial studies D. C. Cronzmeyer measured the concentration of 
oxxygen vacancies in rutile single crystals on the basis of weight loss 
and Hall coefficient measurement showed that the number of conduc-
tion electron was approximately twice the number of oxygen vacancies 
[153]. Further this model was simulated to a helium atom thereby 
calculated the first and second ionization energies to be 0.75 eV and 
1.64 eV respectively. This result was in corroboration with the experi-
mental observation of two visible band tails extending up to IR region 
of the electromagnetic spectra. It was also observed that as the number 
of oxygen vacancies increased, the thermal ionization energy decreased 
due to the interaction of closely spaced donor centers. However 
Cronzmeyer could not give much evidence for the decrease in thermal 
ionization energy with oxygen vacancies [71,153].

Chen et al. followed spectroscopic analysis of high pressure and high 
temperature annealed hydrogenated black TiO2 as well as ab initio DFT 
calculations based on a model of hydrogenated large TiO2 cluster, 
\[\text{Ti}_{218}\text{O}_{436}\text{H}_{70}\] [154]. They compared the spectroscopic data with pris-
tine TiO2 and DFT outputs with that of a less hydrogenated system, 
\[\text{Ti}_{121}\text{O}_{220}\text{H}_{12}\]. It was reported that the surface of the \[\text{Ti}_{218}\text{O}_{436}\text{H}_{70}\] 
cluster had a disorder layer consisting of partial Ti-O and O-H bonds 
retaining a crystalline anatase core. In the XPS spectra the presence of 
pristine TiO2 exactly resembled that of black TiO2 indicating that black 
TiO2 did not possess Ti3+. This result pointed that the valence band 
maximum was not contributed by Ti3+ instead the additional energy 
levels were formed by the presence of hydrogen. Much more evidences 
of absence of Ti3+ was also confirmed with soft X-ray absorption and X-
ray emission spectroscopy. \(^1\)H NMR spectra of pristine TiO2 and black 
TiO2 were slightly differed with two additional peaks at a chemical shift 
around 0 ppm corresponded to the extra hydrogen in the disordered 
surface layer of black TiO2. In the FTIR spectra of black TiO2 a signal at 
4500 cm\(^{-1}\) was observed corresponded to H-H stretching vibrations 
indicative of trapped H2 molecules in the crystal core or in the dis-
ordered surface. Computational and experimental calculations point to 
the sole contribution of hydrogen induced disordered layer which cre-
ated additional mid gap levels responsible for the extended absorption 
up to IR region [154]. Raghunath et al. also observed the similar band 
structure modifications using DFT + U calculations [155]. Apart from 
these many reports point to the formation of Ti3+, which was also re-
sponsible for the enhanced absorption. Incorporation of hydrogen on 
TiO2 surface bound to the lattice oxygen and formed Ti-OH groups 
thereby an electron was trapped in Ti site [156]. This extra electron 
contributed to the formation of Ti3+ and gave rise to mid gap energy 
levels. Finazzi et al. studied effect of this extra electron and that of 
oxxygen vacancy in band structure modifications of black TiO2. They 
concluded that the conduction band minimum was lowered to about 
1 eV which was associated with Ti 3d orbitals [156]. Wang et al. in-
vestigated the effect of Ti3+ in reduced rutile TiO2 which possesses a 
blue color [157]. In pristine rutile TiO2, Ti ions are in slightly distorted 
occtahedral site leading to the splitting of 3d orbitals into t2g (lower energy) 
and Eg (higher energy). Here t2g contributes to the conduction band 
minimum while O 2p contributes to valence band minimum. On the other 
hand the t2g orbitals of Ti3+ self-doped system of the reduced 
rutile TiO2 experience Jahn Teller distortion, consequently split into 
two energy levels (Fig. 18a). The lower energy level (dxy) constitutes 
one electron act an excitation center near the conduction band 
minimum. The corresponding d-d transition contributed to the visible 
light absorption and consequent blue color (Fig. 18b) [157].

Recently Nandasiri et al. systematically studied the thermal stability 
of H-implanted black TiO2 [158]. At low temperature (\(\sim 373 \text{K}\)), hy-
drogen implanted into rutile TiO2 (1 1 0) diffused into the surface and is 
completely depleted from the near-surface region (\(\leq 800 \text{ nm}\)) by 523 K. 
The outward diffusion and depletion of H from TiO2 is accompanied by 
extensive surface reduction within the probe depths of X-ray photo-
electron spectroscopy (XPS) and ultraviolet photoelectron spectroscopy 
(UPS). Due to reduction, most likely, the reaction of H with surface 
oxxygen occurs followed by formation and desorption of water. The 
presence of surface Ti3+ persists until the thermally induced surface-to-
bulk diffusion of Ti3+ interstitials is initiated above 550 K. Nuclear 
reaction analysis (NRA) determines the hydrogen depth profiles as a 
function of annealing temperatures as shown in Fig. 19. The as
S.G. Ullattil et al.  

Table 1  
Synthesis, properties and applications of black TiO₂

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<td>1</td>
<td>High pressure H₂ treatment</td>
<td>Anatase</td>
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<td>Photodegradation of Methylene Blue (MB) and phenol</td>
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<td>Solvothermal method followed by high pressure H₂ treatment</td>
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<td>Nanoporous</td>
<td>V_o, Ti^3+, Ti^4+</td>
<td>Photocatalytic Decomposition of Rhodamine H2 generation, Photocatalytic H2 generation</td>
<td>[163]</td>
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<td>80</td>
<td>H2 treatment on protonated titanate nanotube</td>
<td>Anatase, Rutile</td>
<td>Nanoporous</td>
<td>V_o, Ti^3+, Ti^4+</td>
<td>Photocatalytic Decomposition of Rhodamine H2 generation, Photocatalytic H2 generation</td>
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<tr>
<td>81</td>
<td>Hydrothermal method</td>
<td>Anatase, Rutile</td>
<td>Nanoporous</td>
<td>V_o, Ti^3+, Ti^4+</td>
<td>Photocatalytic Decomposition of Rhodamine H2 generation, Photocatalytic H2 generation</td>
<td>[165]</td>
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<tr>
<td>82</td>
<td>Al reduction</td>
<td>Anatase, Rutile</td>
<td>Nanoporous</td>
<td>V_o, Ti^3+, Ti^4+</td>
<td>Photocatalytic Decomposition of Rhodamine H2 generation, Photocatalytic H2 generation</td>
<td>[166]</td>
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<tr>
<td>83</td>
<td>H2 reduction of white TiO2 inverse opals</td>
<td>Anatase, Rutile</td>
<td>Nanoporous</td>
<td>V_o, Ti^3+, Ti^4+</td>
<td>Photocatalytic Decomposition of Rhodamine H2 generation, Photocatalytic H2 generation</td>
<td>[167]</td>
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<tr>
<td>84</td>
<td>Hydrothermal method</td>
<td>Anatase, Rutile</td>
<td>Nanoporous</td>
<td>V_o, Ti^3+, Ti^4+</td>
<td>Photocatalytic Decomposition of Rhodamine H2 generation, Photocatalytic H2 generation</td>
<td>[168]</td>
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<tr>
<td>85</td>
<td>Al reduction</td>
<td>Anatase, Rutile</td>
<td>Nanoporous</td>
<td>V_o, Ti^3+, Ti^4+</td>
<td>Photocatalytic Decomposition of Rhodamine H2 generation, Photocatalytic H2 generation</td>
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<td>86</td>
<td>H2 treatment on protonated titanate nanotube</td>
<td>Anatase, Rutile</td>
<td>Nanoporous</td>
<td>V_o, Ti^3+, Ti^4+</td>
<td>Photocatalytic Decomposition of Rhodamine H2 generation, Photocatalytic H2 generation</td>
<td>[170]</td>
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<tr>
<td>87</td>
<td>Hydrothermal method</td>
<td>Anatase, Rutile</td>
<td>Nanoporous</td>
<td>V_o, Ti^3+, Ti^4+</td>
<td>Photocatalytic Decomposition of Rhodamine H2 generation, Photocatalytic H2 generation</td>
<td>[171]</td>
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implanted hydrogen profile was peaked at a depth of 300 nm [159].
The hydrogen profile was altered or more clearly the peak at 300 nm
was diminished by the annealing treatment at 373 K. During this, little
or no hydrogen was lost from the crystal into the vacuum as shown by
the integrated NRA signal (inset to Fig. 19). Significantly a notable
amount of hydrogen was lost into the vacuum after annealing at 473 K
(inset to Fig. 19). After 473 K annealing, a remnant of the original
profile remained and this signal points to the presence of trapped H at
the structural defects generated during the implantation process.
Within the sampling depth of the NRA experiment, all of the implanted
H were removed after further annealing treatment at 523 K. Due to the
rapid bulk diffusion of hydrogen to its interfaces, followed by deso-
aption (as H2O and H2) and surface reduction, the limited stability of H-
TiO2 was demonstrated. Also according to their previous results the
kinetics of the removal of surface hydrogen (as water) into vacuum,
exceeds that of the diffusion into TiO2 (1 1 0) bulk which emphasizes
the limitation of the thermal processing of H-TiO2 in visible light ap-
lications [158].

Experimental evidences point to the dependence of black coloration
on synthetic strategy. For example Wang et al. synthesized black TiO2
using Al as reductant at different temperatures 400, 500 and 600 °C
[160]. The black TiO2 at 500 °C possessed intense black color, absorb-
ance and photoactivity. When the reductant is the same, the intensity
of black color will depend upon the gas used. For example, when NaBH4
used as a reductant to produce black TiO2, the sample treated at 350 °C
showed maximum black color in presence of Ar gas flow [109] whereas
intense black color was observed at a temperature of 500 °C for N2 gas
flow [161]. The so formed defective TiO2−x was treated at various
temperatures (300–700 °C) under 150 sccm N2 gas flow for 3 h
(Fig. 20). As shown in figure, the transition of color occurred and the
maximum blackness was observed for TiO2-500. In addition as the
temperature increased the intensity of anatase peaks increased.

Another important observation was when Zn used as a reductant,
rutile black TiO2 nanorods were formed instead of the formation ana-
tase black TiO2. The black coloration was increased with the increasing
amount of Zn (from 0.5 to 2.5 mmol) [162]. The color intensity of TiO2
can be varied using laser ablation method with respect to the time in-
terval (Fig. 21) selected. Here the color changes from white to dark blue
as time varies from 0 to 120 min of laser irradiation [127]. It has been
also proved that, by varying the ultrasonication time period, the color
of TiO2 nanomaterial can be varied from white to black [126].

4. Phase, defect states and morphology of black TiO2

The phase and defect states are generally observed by using XRD,
Raman, XPS, EPR, FTIR, NMR, synchrotron X-ray absorption spectro-
scopic techniques [127–132,158–196]. Recently HRTEM images are
also used in detecting the surface defects present on a nanomaterial
along with the morphology [127]. Ti3+ ions and oxygen vacancies are
the common defects which are observed in the surface of a black TiO2
crystal. XRD depicts the crystal phase of TiO2 and some extent of
crystallinity and the incorporation of elements into the crystal lattice
can also be perceived from XRD. We have recently proposed anatase
phase pure TiO2 and the peaks were lesser in number. Interestingly
after the Mn2+ reduction, the XRD peaks were found to be shifted to-
wards higher 2θ. Additionally, the peak texturing in all existing planes
along with new anatase peak formation (Fig. 22) was occurred and
revealed the phase purification activity of Mn2+. It was due to the sy-
nergistic effects of the thermodynamic and kinetic factors which control
crystal nucleation. In addition, the Mn2+ modification tends to speci-
fically lower the Gibbs free energy in the high index anatase (1 0 0 5)
orientation, and thus stabilizes the distinct atomic configuration along
the (1 0 5) plane [115]. The black TiO2 nanoparticles synthesized
through Mg reduction has resulted in anatase/rutile mixed phase along
with other non-stoichiometric titanium oxide phases depends on the
amount of Mg used [138]. As the amount of Mg increased the
crystallinity of the sample decreased. H-R. An et al. observed anatase/brookite bicrystalline phase using XRD analysis [134]. They synthesized the bicrystalline nanoporous black TiO2 through H2 plasma treatment. Later Z. Tian et al. reported hydrogenated TiO2-B phase and it was confirmed through XRD that TiO2-B phase maintained its actual framework even after hydrogenation [140]. C-C. Wang et al. synthesized black TiO2 nanowires through hydrogen thermal as well as hydrogen plasma treatment and the resultant phases were purely rutile [141]. Wang et al. reported that as the temperature increased the intensity of XRD peaks increased which is due to the decrease in defect states and/or increase in crystallinity of TiO2−x [160, 163]. Fan et al. synthesized amorphous TiO2 nanoparticles by hydroxylation followed by ultrasonication but the XRD patterns showed no characteristic peaks of TiO2 under any sonication time interval [126]. Apart from these, no change in XRD pattern was observed between white and black TiO2 reported by Xin et al. (Fig. 23A) [164]. Also for the same materials, no change in Raman spectra were also observed (Fig. 23B) indicating that no modification of the main crystal phase was occurred even though the color of the TiO2 material was changed from white to black [165]. The disordered surface layer present in black TiO2 which is undetectable in XRD can be effectively characterized through Raman spectroscopy.

Leshuk et al. showed the high amount of hydrogenation using Raman spectra [85] where an intense peak at 1354 cm−1 for black TiO2 is ascribed to the Ti-H mode of vibration (Fig. 24A) [166]. Another important study using Raman spectra by Zhang et al. confirmed the presence of lattice disorder in black TiO2 resulting from phonon confinement and non-stoichiometry due to the oxygen vacancy (Vo) doping (Fig. 24B) in black TiO2 which was evidenced by the blue shift of main Raman peak at 147.8 cm−1 to higher wave number, 153 cm−1 along with peak broadening as indicated [167].
In the Raman spectra of magnesiothermal Ar treated black TiO$_2$ (Fig. 25), the peak exhibited a blue shift along with peak broadening compared to the commercially available TiO$_2$ annealed in Ar atmosphere [93]. These features were observed earlier in the case of modified TiO$_2$ nanoparticles where non-stoichiometry and defects states attributed with the structure [168].

In the Raman spectra of black TiO$_2$ (B)/anatase bicrystalline nano fibers, six Raman active modes of the anatase phase (3Eg + 2B1g + A1g) were detected indicating that anatase phase is the main component of these TiO$_2$ samples [132]. In addition to these peaks, two weak bands are also seen from 220 to 260 cm$^{-1}$ which corresponded to Raman active modes of TiO$_2$ (B) and is shown inset of Fig. 26[169,170].

Existence of defects such as Ti$^{3+}$ and oxygen vacancies present in a material can be more clearly perceived from X-ray photoelectron spectroscopy (XPS) [77,115], electron spin resonance spectroscopy (ESR spectroscopy) [90] and synchrotron X-ray absorption–emission photoelectron spectroscopic [154] techniques. In the most of the XPS studies conducted so far, Ti$^{3+}$ defects in black TiO$_2$ are seen as a result of hydrogen treatment [77], chemical reduction, electrochemical reduction [125], microwave treatment [115], Al reduction [110], gel combustion strategy [131] and hydrogen plasma treatment [171]. During H$_2$ plasma treatment on electrospun nano fibers along with Ti$^{4+}$ and Ti$^{3+}$, Ti$^{2+}$ has also been detected at the surface of black TiO$_2$ [171].

Wang et al. manipulated the higher wavelength solar absorbing black TiO$_2$–x H$_x$ (~83%) which was further characterized by FTIR and NMR spectroscopic techniques to confirm the structural changes that has been formed due to hydrogenation [102]. In the FTIR analysis (Fig. 27a) the presence of Ti-O-Ti bond of TiO$_2$ is clearly visible and in the longer wavelength range new peaks were originated at 3645, 3670 and 3685 cm$^{-1}$ due to hydrogenation (Fig. 27b). These results were attributed to tetrahedral coordinated vacancies and are assigned to the presence of Ti$^{4+}$-OH. Another new peak located at 3710 cm$^{-1}$ was ascribed to the terminal -OH groups indicating the embedded H atoms with in the TiO$_2$ network [172–173].

Comparatively large band width was observed for hydrogenated TiO$_2$ may be due to incorporation of H at the bridging sites of TiO$_2$ or due to the change in environment of bridging sites at different planes [174]. The additional signals at chemical shifts, δ = 0.4 and 0.01 ppm are due to respectively terminal and internal hydroxyl groups of anatase (Fig. 27c and d) [175]. According to Chen et al. [154] the chemical shift values of terminal and internal hydroxyl groups of anatase were δ = 0.73 and δ = 0.03 ppm respectively. The peaks were of low intensity indicated the low concentration of H that has been incorporated and the new peaks were possibly due to dynamic exchange mechanisms such as rapid isotropic diffusion and rapid exchange between similar proton environments [176].

Almost similar XPS (both Ti2p and O1s) were observed for both pristine and hydrogenated TiO$_2$ [102]. The Ti2p centered at 458.5 and 464.3 eV (Ti2p$_{3/2}$ and Ti2p$_{1/2}$) typical for Ti$^{4+}$-O bond of TiO$_2$ [177]. An additional broad peak at 457.1 eV was also observed which is attributed to surface Ti-H bonds [178]. Interestingly negligible effect on band edge position (2.05 eV) was also noticed [179]. In addition the PL spectra showed a notable decrement in PL intensity for TiO$_2$–x H$_x$ as compared to the pristine TiO$_2$ confirmed the incorporation of H into the crystal lattice of TiO$_2$ (Fig. 29). Similarly the VB spectra showed the same fashion i.e. the same band edge position was explained by Leshuk et al. According to them hydrogenation followed by annealing had no effect at the band edge position of TiO$_2$ even though they had explained the disordered structure using Raman spectra [85]. Similarly no effect on Ti2p spectra was observed after hydroxylation ultrasonication reported by Fan et al. [126].

According to our previous report we have developed oxygen richness at the surface of yellow TiO$_2$ and was evident from XPS [115]. Whereas on Mn reduction the yellow oxygen rich TiO$_2$ transformed into oxygen vacancy rich black anatase TiO$_2$. The Ti2p$_{3/2}$ peak (460.05 eV) of oxygen rich TiO$_2$ was colossally decreased to 457.65 eV which suggested the oxygen vacancy richness forcefully applied on oxygen rich environment (Fig. 29) [115].

Naldoni et al. introduced surface defects on P25 TiO$_2$ with band gap energy 3.25 eV. The Density of States showed that the reduction in band
gap energy of black anatase TiO$_2$ owing to the creation of mid-gap energy levels within the band gap [88]. They explained that the major absorption onset of black TiO$_2$ was located at 0.6 eV. Also the band tail was blue shifted towards $-0.3$ eV. These observations pointed that surface disorder induced a striking band gap narrowing of 1.85 eV (Fig. 30) [88].

Microscopic techniques (SEM and TEM) were used to derive the morphology and defect states in black TiO$_2$. Different type of morphology such as mesoporous, nanoporous and core-shell nanostructures morphologies comprising nanotubes [124,98], plates [180], sheets [114,212,215], wires [140,141,225], films [117,129,181–183], fibers [171,184], inverse opals [164], spheres [106] arrays [185], cage [146], flower [137], leaves, spike [186], thorns [143], and belt [187], of black TiO$_2$ were formed as a result of different synthesis methods used for preparation. Some important morphologies obtained were shown in Fig. 31.

Black TiO$_2$ nanoparticles prepared through high pressure hydrogenation and high temperature aluminum reduction distinctly possessed a crystalline core/amorphous shell structure [154,110]. The amorphous shell consists of disordered surface layer containing oxygen vacancies whereas the crystalline core has trivalent titanium ions dispersed in it. The excellent optical absorption features correspond to the disordered surface layer and the consequent photocatalytic activities on crystalline core are the outcome of the synergy between the shell and the core [188]. The first report on black TiO$_2$ by Chen et al. clearly explained the defective surface layer of hydrogenated TiO$_2$ by using HRTEM (Fig. 1) [77]. Since then most of the researchers applied TEM and HRTEM as a supporting tool to explain the core-shell structure, usually crystalline core-amorphous shell structure [86,105,110], i.e. the defects generally associated with the shell of a nanoparticle. Recently L. Li et al. observed microwave absorption features on black TiO$_2$ nanoparticles which possessed a unique core-shell structure. Prof. Geoffrey A. Ozin and coworkers reported comparatively thicker amorphous shell of TiO$_2$$_{x}$ through Mg reduction method than that resulted in hydrogenation or aluminum reduction [138]. Our group have found the defect state within the core of the black TiO$_2$$_{x}$ nanoparticle using HRTEM as shown in Fig. 32.

Xia et al. explained the surface defect states using HRTEM along with the line analysis [188]. From HRTEM image (Fig. 33A), white TiO$_2$ is completely crystalline with well-defined lattice fringes and the lattice fringe distance was found to be 3.536 Å which is characteristic of anatase phase and is uniform throughout the nanocrystals [188]. The statement is evident from the line analysis (Fig. 33C), whereas the black TiO$_2$ nanocrystal has a crystalline core and amorphous shell structure (Fig. 33B). The core shows clearly resolved (1 0 1) lattice plane of anatase with lattice fringe distance of 3.515 Å, which is consistent with the line analysis diagram (Fig. 33D). At the amorphous outer layer, the distances between adjacent lattice planes are highly distorted, e.g. 2.983 Å, 4.203 Å, and 6.747 Å (Fig. 33D) [188].
W. Hu et al. could synthesize mesoporous black TiO$_2$ hollow nano spheres with highly crystalline pore-walls and surface disorders [189]. Surface disordered shell and Ti$^{3+}$ dispersed in hollow structure frameworks imparted the enhanced optical absorption as well as suppression of recombination of charge carriers. Similar observations were also reported by K. Zang in which the mesoporous black TiO$_2$ nanosheets were synthesized using a low cost biotemplate [89]. Electro-conducting mesoporous anatase black TiO$_2$ nanoleaves were reported
by Y. J. He [190]. They focused on its electrochemical applications and pointed out that the enhanced electro-conductivity is due to the presence of trivalent titanium ion. Prof. W. Zhou and coworkers fabricated three-dimensional nanosheets formed out of MoS2 sandwiched between black TiO2 nanosheets [191]. The introduction of a layered oxide within the framework of the nanosheets significantly contributed to the efficient charge separation of photogenerated charge carriers [191].

Black TiO2 nanowires were particularly noted for their large specific surface area and minimalized recombination rate for the photogenerated charge carriers due to limited diffusion distance as well as fast charge transport with the added advantage of enhanced optical absorption properties [192]. Black TiO2 nanomaterials with a tubular morphology can be easily obtained even at low temperature and ambient pressure because pristine TiO2 nanotubes have the capacity to store molecular hydrogen [98]. L. Han et al. synthesized anatase black TiO2 nanotubes using hydrothermal method [98]. When the synthesis temperature was beyond 150 °C the anatase nanotubes started converted to black TiO2-B nanobelts and at 210 °C complete transformation could be observed. As the temperature increases the nanotubes intertwined with each other losing their molecular hydrogen incorporation capability leading to a nanobelt morphology. Zhu et al. designed black TiO2 nanocages having supreme optical absorption features consequent to the internal light trapping effect [146]. Additionally these nanocages possessed mesopores which facilitates the permeation of water vapor. Recently MoS2 nanoflower coated nitrogen doped TiO2 was reported [191]. It has a nanoflower ball morphology with core-shell structure. The effective separation of photogenerated charge carriers in N-TiO2−x@MoS2 was attributed to the synergistic effect of dopants and introduction of MoS2.

Presence of Ti3+ in the crystal structure of black TiO2 nanoparticles contributes to the enhanced light harvesting capability [193–195]. As evidenced in several reports, the amorphous shell that surrounds the crystalline core is due to Ti3+ and/or Vo’s [86,105]. Generally at higher temperature these defects states may disappear and the light harvesting capability, in particular the photocatalytic efficiency may be decreased. Recently an advanced TEM analysis was used by Tian et al. for investigating the structure and formation of black TiO2 [196] where they used a pulsed laser vaporization (PLV) technique to synthesize amorphous ultra-small rutile nanoparticles followed by annealing at 970 K leading to rutile core-black TiO2 shell nanostructure (Fig. 34) [196]. From the atomic-resolution high-angle annular dark-field (HAADF) image of a rutile NP viewed in the (0 0 1) direction (Fig. 34.1) showed that there was a transition region, connecting the disordered Ti2O3 shell to the perfect rutile core [196]. Nano beam electron diffraction (NBED) was also employed for further structural investigations (Fig. 34.2) and the rutile core structure exhibited a 4-fold symmetry which is the characteristic of perfect rutile. As the surface approached, both kinetically and dynamically forbidden reflections in pure rutile (1 0 0) in the (0 0 1) zone axis) was appeared 2–4 nm away from the vacuum undoubtedly indicated the deviation of Ti from the octahedral symmetry and a trace amount of oxygen vacancies. Furthermore increased oxygen vacancy at the surface led towards the deviation from rutile phase represented by the rotation of (0 2 0) and (0 2 0) reflections [196].

Tominaka et al. has reported a topotactic reaction for the transformation of rutile-type TiO2 to corundum-type Ti2O3 during low-temperature reduction [197]. This reaction successfully retained the crystal habit of the rutile parent as demonstrated by the conversion of TiO2 nanorods into Ti2O3 nanorods. Unlike the Ti2O3 synthesized by conventional route, topotactically synthesized Ti2O3 exhibited a semi-metallic/metallic electronic conduction, which indicated that the method is promising to access narrow- or zero band gap titanium-based oxide materials which can be used in a variety of electronic applications [197].
5. Applications of black TiO₂

Nano TiO₂ and its modifications were studied extensively for its various functional applications [198–200]. Black TiO₂ is now one of the most attractive candidate in the area of photocatalysis, dye sensitized solar cells, supercapacitors, batteries and even in photothermal therapy mainly due to their wide area absorption and thereby narrowed band gap energy. Since it is one of the unequivocally established candidate in...
several applications, to date applications that has been reported on black TiO$_2$ are explicitly explained in the following sections.

5.1. Photodegradation

The first reported black TiO$_2$ by hydrogenation was employed in photodegradation of phenol and methylene blue [77]. Leshuk et al. also used methylene blue (MB) as model system for photocatalysis [85]. Ullattil et al. have demonstrated the oxygen vacancy rich black anatase TiO$_2$ for solar photocatalysis [115]. All these studies experimentally proved that the black anatase TiO$_2$ that has been synthesized was highly active than the commercially available photocatalyst Degussa-P25 for MB degradation. For example, Xin et al. reported a 30-fold enhancement in visible-light decomposition of methylene blue compared with the commercial sample P25 using black TiO$_2$ prepared by solvothermal assisted method [161].

The black plate like brookite TiO$_2$ with core/disordered shell structure (TiO$_2$ @ TiO$_2$–$x$) through Al reduction by Zhu et al. facilitated photodegradation under visible light towards the photodegradation of methylene blue (MB) and methyl orange (MO) [180]. MO degraded completely within 20 min under solar light irradiation and MB degraded 50% in 3 h under visible light using black brookite TiO$_2$ photocatalyst, points to the enhanced activity arisen due to the modifications in TiO$_2$. Black TiO$_2$–B and black anatase TiO$_2$ have shown enhanced MO photodegradation as compared to commercially available P25 under visible light irradiation [94]. Wang et al. examined the photoactivity of black TiO$_2$ by using MO as model system in both acidic (pH 1) and in neutral (pH 7) media [160]. They have found that the degradation rate in acid medium was more than to that in neutral medium as shown in Fig. 35. They have also analyzed the recyclability of the most efficient photocatalyst, T500 and found their intact activity even after five consecutive cycles [160].

Lin et al. have presented a series of nonmetal doped black TiO$_2$ nanoparticles for the photodegradation of methyl orange and H$_2$ generation [113]. Laser modified black TiO$_2$ nanostructures have shown enhanced photodegradation of rhodamine B dye whereas P25 has no photoactivity under the same experimental condition using a light source of green LED with 3.7 V voltage, 25 mA current and 520 nm wavelength [127]. By using a red LED (Voltage = 2 V, Current = 45 mA) result was the same but the photoactivity was decreased to a large extent for the black TiO$_2$ [127]. The same model system has been degraded by black TiO$_2$ that has been prepared by hydrogen plasma assisted chemical vapor deposition [103].

Samsudin et al. successfully employed the hydrogenated black TiO$_2$ nanoparticles for atrazine degradation [201]. The Al reduced black TiO$_2$ has found a tremendous photocatalyst for the degradation of MO and phenol [110]. According to Fan et al. hydroxylated TiO$_2$ prepared through ultrasonication demonstrated high photocatalytic activity for the degradation of acid fuchsin [126].

5.2. Hydrogen generation

Generating hydrogen, most ecofriendly fuel, from water using abundant solar radiation assisted by the complete solar spectrum absorption features of TiO$_2$ can be considered as a sustainable energy solution and many attempts were made to address its basic limitations,
viz, as wide band gap and rapid charge carrier recombination [202,203]. Black TiO2 has been an unequivocally established as a potential candidate in the process of hydrogen generation via photocatalytic as well as photoelectrochemical route. Black TiO2 possesses suitable band structure for hydrogen generation. The conduction band minimum of the black TiO2 nanoparticles is thermodynamically and kinetically favorable for water reduction.

5.2.1. Photocatalytic water splitting by black TiO2

After the identification of black TiO2 as a potential candidate for photocatalysis, extensive studies were carried out to utilize its wide absorption features and efficient charge separation properties in hydrogen generation [204–208]. According to Wang et al. as the Al reduction temperature was increased, the amount of H2 generation increased [110]. More specifically the hydrogen gas produced was 8.5 times to that of pristine TiO2. The same black TiO2 was found excellent photo electrochemical electrode that exhibited 1.7% solar to hydrogen efficiency [110]. Atmospheric H2/Ar annealing was applied by Liu et al. for the synthesis of black TiO2 nanotubes that showed a high open circuit photocatalytic hydrogen production rate [90]. After 20 days of high pressure hydrogen treatment on Degussa P25 paved the way to 3.94 mmol g−1 h−1 H2 evolution rate in methanol solution [86].

Zhao et al. demonstrated black rutile nanorods through Zn reduction and the catalyst was generated H2 from the water-methanol solution both under UV and visible light irradiation [162]. Zhou et al. achieved ordered mesoporous black TiO2 with high thermal stability [184]. Here larger pore size and higher surface area of mesoporous black TiO2 paved the way to high solar driven hydrogen production rate. The pristine mesoporous TiO2 had shown a hydrogen production rate of 76.6 μmol h−1 whereas the ordered mesoporous black TiO2 showed a larger production rate of 136.2 μmol h−1 which was almost twice to that of pristine mesoporous TiO2. The cycling tests of the photocatalytic hydrogen generation under AM 1.5 and under visible light were also conducted to confirm the reusability of the photocatalyst. Lepcha et al. reported electro spun black TiO2 nano fibers by hydrogen plasma treatment [171]. These nano fibers showed 10-fold more photo electrochemical performance than pristine TiO2. Yang et al. reported an excellent H2 production by S doping on a core-shell nanostructured black rutile TiO2 [209]. The photocatalyst showed 1.67% solar to hydrogen conversion efficiency (Fig. 36) [209].

5.2.2. Photoelectrochemical (PEC) water splitting

The black TiO2 nanowires prepared by Wang et al. showed notable photoelectrochemical water splitting property with Ag/AgCl system. Here also improved hydrogen generation was attributed to the enhanced charge separation and high charge density [87]. Core-shell black TiO2 nanosheets obtained by NH3 plasma had significant photocurrent density [211]. Similarly TiO2 produced by electrochemical method and chemical reduction method reported to high photocurrent density and photoconversion efficiency [89,108].
Apart from photoelectrochemical water splitting, black TiO$_2$ films were used for the photoreduction of CO$_2$ by Quingly et al.\cite{181}. Due to wide area absorption and defect states present (Ti$^{3+}$ and oxygen vacancies) of black TiO$_2$, selective formation of CO and CH$_4$ were occurred hundred times higher as compared to conventional TiO$_2$ (Degussa P25) (Fig. 38) \cite{181}. Another important study is by pursuing disorder engineering at the surface of 2D nanosheets of white TiO$_2$ by NaBH$_4$ treatment followed by calcination at 220–300°C in N$_2$ atmosphere resulted black TiO$_2$ nanomaterials. Its photocurrent (80 µA cm$^{-2}$) was four times more than that of the white TiO$_2$ and it
presented a higher solar-driven hydrogen production rate of 400 μmol h⁻¹ [212]. Hu et al. demonstrated a stable mesoporous black TiO₂ hollow spheres with relatively high surface area as compared to black TiO₂ nanoparticle has shown 241 mmol h⁻¹ 0.1 g⁻¹ solar driven hydrogen generation which was twofold and three fold more active than that of black TiO₂ nanoparticles and pristine TiO₂ hollow spheres respectively [189].

Recently black TiO₂ nanomaterials was used as a coating on Cu for improving CO₂ photoreduction [213]. The coating was used to restrain the rapid oxidation of Cu with surroundings. The photocatalytic activity for Cu@TiO₂ (~4%Cu) reaches 1.7 times of that for its counterpart, bare black TiO₂. The improved photoactivity is attributed to Cu embedded in TiO₂, which created oxygen vacancy sites within the lattice through metal-oxide interaction [213].

Annealing in air, annealing in nitrogen and balanced annealing using H₂-N₂ treatment on TiO₂ nanotube arrays were carried out by Carlson et al. for the bacterial disinfection of waterborne bacteria [214]. The absorption and efficiency was found more in the case of H₂-N₂ treated nanotube arrays (black TiO₂ nanotube) [214]. Black brookite single crystalline nanosheets were also employed in photocatalytic CO₂ reduction [215]. Here the excess Ti³⁺ defect states in the bulk of brookite nanosheets led the way to increased solar energy absorption and thereby increased photocatalytic activity [215].

5.3. Dye sensitized solar cells (DSSC)

Another important application of black TiO₂ was in field of DSSC. Recently black TiO₂-x was employed in DSSC as a counter electrode individually and as composite of black TiO₂-x with carbon nanotube [216]. A photoconversion efficiency of 5.71% was achieved. The defective black TiO₂-x showed wide area absorption (Fig. 39) and oxygen vacancies of TiO₂-x extended the photo response of TiO₂ from the UV to the visible light region helped to improve the photocconversion efficiency. These defective black TiO₂-x and composite TiO₂-x/CNT can be used as an effective alternative to the traditional Pt counter electrode in DSSC [216]. A very recent report showed that Mn²⁺ incorporation in TiO₂ nanoparticles has a black color and the resulted black TiO₂ alone has been efficiently worked as a photoanode material in DSSC [217].

5.4. Li ion batteries

Surface amorphized TiO₂ nanomaterials significantly contributed to enhance the performance of Li ion rechargeable battery [218–220]. Black TiO₂ nanomaterials are also considered as potential candidates for electrode material for Li ion batteries. Black TiO₂ obtained by the hydrogenation on normal white TiO₂ improved the electronic conductivity and oxygen vacancy richness for its better application in Li ion batteries [92]. Yan et al. investigated the performance of fast Li storage of Ti³⁺ doped hydrogenated black TiO₂ [104]. The fast Li storage was due to the pseudocapacitive Li storage at the surface and the pseudocapacitive effect was due to the presence of defect states such as Ti³⁺ and oxygen vacancy states [104]. Myung et al. achieved black anatase TiO₂ with an electro-conducting Ti³⁺ (incorporation of H and N) [101]. This black anatase nanomaterial showed a very high electrical conductivity of 8 × 10⁻² S cm⁻¹. The presence of the Ti³⁺ ion narrowed the band gap towards 1.8 eV that enabled a quick lodging of Li⁺ into the anatase TiO₂ structure and subsequent extraction. The material shows promising retention percentage of discharge capacity in charge-discharge cycles [101].

Bae et al. reported different weight percentage of TiO₂-x, coated Si/ SiO₂ nanosphere as anode material for Li ion battery [221]. The electroconductive TiO₂-x-coating enabled high coulombic efficiency, thermal reliability and reversible capacity. A very high reversible capacity of 1200 mAh g⁻¹ with an extraordinary recycling rate up to 100 cycles was achieved. The TiO₂-x layer art on the surface of Si/SiO₂ nanosphere can further take up more oxygen from the Si/SiO₂ phase leading to increase in coulombic efficiency and reversible capacity of the TiO₂-x @ Si/SiO₂ nanosphere. This reductive nature enabled narrowed band gap that ensures sufficient electrical conductivity leading to higher efficiency (Fig. 40) [221].

TiO₂-x nanotube arrays have been synthesized by Eom et al. through thermal conversion treatment of amorphous TiO₂ nanotubes under hydrogen atmosphere were implemented as an efficient material for Li ion batteries due to their high electronic conductivity facilitated by increased defect states of oxygen vacancies and Ti³⁺ ions [185].

5.5. Na ion batteries

Resembling high concentration of oxygen vacancy sites and Na ion diffusion length in the nanostructure, black TiO₂ was employed as an anode in sodium-ion batteries [222]. The black TiO₂ that has been synthesized was occupied with oxygen vacancies both at the surface and in bulk. A high reversible specific capacity of 207.6 mAh g⁻¹ at 0.2C, retained 99.1% over 500 cycles at 1C and still maintained 91.2 mAh g⁻¹ even at the high rate of 20C. After the charge-discharge process of over 500 cycles at 1C, the capacity of 185.1 mAh g⁻¹ was maintained with a retention of as high as 99.1%, indicating a long cycling stability. Here lower sodiation energy barrier of anatase with oxygen vacancies enabled a more favorable Na intercalation into black anatase TiO₂ [222].

5.6. Al ion batteries

Black mesoporous anatase TiO₂ nanoleaves synthesized via solution plasma processing was employed in Al ion batteries by He et al. [190]. The initial charge capacity of TiO₂ nanoleaves corresponding to Al₀.₂₇TiO₂ was comparatively higher (278.1 mAh g⁻¹) than that of anatase TiO₂ nanotube arrays. Black TiO₂ nanoleaves possessed a high Al³⁺ storage performance as a consequence of ordered nanoparticles which enhances the bulk intercalation and the interfacial storage capacities. In addition to this, they compared the rate performance of commercial white anatase TiO₂ and black anatase TiO₂ nanoleaves at a current density of 0.1 A g⁻¹, the reversible rate capacity of commercial white TiO₂ is 62.6 mAh g⁻¹ and that of black TiO₂ nanoleaves is 259.7 mAh g⁻¹ with excellent recyclability (Fig. 41). This superior reversible rate capacity of black TiO₂ was associated with the conductive Ti³⁺ which enables the fast electron transfer [190].

5.7. Supercapacitors

Highly ordered black TiO₂ nanotube arrays demonstrated a highly efficient electrode material for supercapacitors [122]. Self-doped black
TiO$_2$ with narrowed band gap energy and thus low resistivity enabled highly efficient supercapacitor. Here as a result of this electrochemical doping, a nearly rectangular-shaped cyclic voltamogram was obtained for the TiO$_2$ samples comparable with ideal capacitors [223]. Black TiO$_2$ nanotube arrays synthesized by Kim et al. used as a supercapacitor as well as an oxidant generating anode [224]. The comparison of pristine TiO$_2$ with this black TiO$_2$ using cyclic voltammograms (Fig. 42) revealed a significantly higher charging current for black TiO$_2$ than the pristine TiO$_2$. It is well clear that oxygen was evidently generated on the black TiO$_2$ under a potential of 1.2 V, whereas no oxygen evolution reaction was observed on the pristine TiO$_2$. These studies proved that the potential of black TiO$_2$ both as a supercapacitor and an oxidant generating anode [224]. Zhi et al. fabricated a solid state supercapacitor (ASSSC) using black TiO$_2$\textsuperscript{−}x:N decorated 2D NiO nanosheets.
as positive electrode and mesoporous graphene as negative electrode (Fig. 43) [112]. The 2D NiO nanosheets were pseudocapacitive material and black TiO$_2$-$x$N as conductive agent. This flexible ASSSC possessed a high energy density of 47 Wh kg$^{-1}$ in a voltage region 0–1.6 V [112].

5.8. Surface enhanced Raman active Scattering (SERS) substrate

Y. Shan et al. introduced wafer scale silver deposited black TiO$_2$ nanowires as substrates for Surface-Enhanced Raman Scattering (SERS) technique [225]. The material induced superior chemical enhancement compared to other semiconductors and comparable to the noble metal substrates.

5.9. Solar desalination

G. Zhu et al. designed black TiO$_2$ nanocages with mesopores for water desalination. Solar desalination is the universal accepted method which will effectively address water scarcity problem [146]. Solar desalination works on the principle air-water interface solar heating. Here solar irradiation is selectively absorbed by the air-water interface thereby eliminating bulk heating of water. These material possessed enhanced absorption due to light trapping effect of the nanocage morphology. The well crystallized nanograins associated with the nanocages promoted heat transfer from titania to water. Along with the mesopores induced the permeation of water vapor with an added advantage of light to heat conversion. The process is schematically represented in Fig. 44. M. Ye et al. also developed black TiO$_2$ nanoparticles for desalination through solar water evaporation [138]. They conducted experiment with black TiO$_2$ coated on a stainless steel mesh followed by superhydrophobization through fluoroalkylation and finally solar water evaporation was achieved [138].
5.10. Photothermal therapy

Ren et al. used black hydrogenated TiO₂ as photothermal agent for cancer photothermal therapy [226]. To increase its stability in physiological environment, polyethylene glycol (PEG) coating was implemented and a photothermal conversion efficiency of 40.8% was achieved. The toxicity and cancer therapy effect of polyethylene glycol (PEG) coated black TiO₂ was evaluated in vitro and in vivo. Systematic studies revealed that the infrared-irradiated PEG coated black TiO₂ exhibited low toxicity, high efficiency as a photothermal agent for cancer therapy. Its toxicity was evaluated in vivo in mice and found no significant changes in its routine and internal organs. By applying tumor cells (4T1 cell line of murine breast cancer) in mice, the PTT activity was examined and found interestingly that the tumor cells were disappeared after 14 days of treatment using PEG coated black TiO₂ along with laser (Fig. 45) [226]. Another important study in this field was reported by Mou et al. where a single NIR laser (wavelength = 808 nm, power density = 1 W cm⁻²) induced multifunctional theranostic nano platform based on black TiO₂₋₄ has been constructed for dual-modal imaging-guided cancer therapy both in vitro and in vivo [227]. The tumor was completely eliminated in 2 days with no recurrence for 20 days investigation, attributed to the photothermal-photo dynamic synergistic effect [227].

6. Summary and outlook

As the growing interest of the scientific community towards the renewable energy resources, especially sun light, fueled the exploration of black TiO₂ as an excellent sunlight harvester. Its applications in many other areas are also emerged. Various synthetic strategies of black TiO₂ nanomaterials have been developed and each method has its own advantage in designing its morphology, optical and functional properties. Origin of black coloration, presence of defects and their applications in various fields such as photodegradation, solar water splitting for hydrogen generation, dye sensitized solar cells, supercapacitors, batteries and therapeutics have been reviewed. Irrespective of the presence or absence of defective surface layer of black TiO₂, it can obviously act as a light harvester due to its wide area absorption from UV region to IR region. In addition, its use in medicinal applications namely in photothermal and photodynamic theranostics may lead to an effective and tremendous material having applications in all hot areas. Black TiO₂ nanomaterials is appeared as the right candidate which can absorb the entire solar spectrum from UV to IR region, may in future will lead towards the maximum technological development, particularly in the area of sunlight harvesting. In addition, the confinement of midgap states in black TiO₂ provides trapping centres for photogenerated charge carriers which inhibits the recombination, thereby enhancing the catalytic activity beneficial for the environmental and energy related applications. Novel applications of black TiO₂ are arising continuously. Black TiO₂ is identified as Microwave Absorbing Materials (MAMs). The symbiosis of crystalline-core and amorphous-shell in black TiO₂ attributes the origin of microwave absorption [128]. The similar feature was also utilized in designing Surface Enhanced Raman Scattering (SERS) Substrate in which the enhancement of the photogenerated charge carrier density reinforces the chemical and electromagnetic characteristics [225]. Another remarkable achievement is in the field of Self-Cleaning Coatings through photocatalytic disinfection [228]. Since the ultimate utilization of the universal energy source, sunlight, is a tedious one, we hope that a black TiO₂ material can be able to fulfill the energy needs of the present scenario. Therefore, further attention should be given to the performance of black TiO₂ in real industrial practice to develop new technologies.

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