Hierarchically Porous, Biphasic, and C-Doped TiO₂ for Solar Photocatalytic Degradation of Dyes and Selective Oxidation of Benzyl Alcohol

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ABSTRACT: Macroporous TiO₂ monoliths were synthesized by self-sustained combustion reactions of molded pellets made up of a mixture of TiCl₄ as a precursor, urea as a fuel, ammonium nitrate as an oxidizer, and starch as a binder. The porous TiO₂ monoliths were found to be a heterostructure of anatase and rutile phases, in addition to being doped with carbon. Variation in the amount of starch yielded porous monoliths of different anatase–rutile ratios (increasing rutile component from 0 to 40%) but comparable Brunauer–Emmett–Teller (BET) surface area (≈30 m² g⁻¹). The porous monoliths obtained, where the TiCl₄/starch mass ratio was 2.17, exhibit exceptional photocatalytic activity in the degradation of dyes (methylene blue and methyl orange) and selective oxidation of benzyl alcohol to benzaldehyde under natural sunlight. The synergistic combination of high surface area, porous network, lowered band gap due to heterostructured anatase–rutile mixtures are generally formed above 600 °C, yielding TiO₂ samples that deviate from nanoregime, and hence reduce the surface area, leading to a decrease in photocatalytic efficiency.6,26 It would be ideal to improve the efficiency of materials similar to Degussa P25.5,19 Major concerns in the preparation of compositions similar to Degussa are: (1) anatase–rutile mixtures are generally formed above 600 °C, yielding TiO₂ samples that deviate from nanoregime, and hence reduce the surface area, leading to a decrease in photocatalytic efficiency29 and (2) nitrogen doping stabilizes the anatase phase at higher temperatures, thus preventing the formation of a biphasic mixture.30

1. INTRODUCTION

TiO₂ photocatalysts1 have been of interest, as they facilitate the photocatalytic degradation of organic pollutants,2–6 selective organic transformations,7–11 and hydrogen generation by photocatalytic water splitting.12–14 Adsorbed radicals formed by photogenerated electron–hole pairs at the photocatalyst surface cause photocatalytic reactions.15,16 TiO₂ exists in three polymorphic forms—anatase, rutile, and brookite.1,15,16 The anatase phase has been found to exhibit higher photocatalytic efficiency.17,18 While anatase with a band gap of 3.2 eV is confined to absorption of UV light, rutile with a lower band gap (3.0 eV) can absorb visible light. However, low surface area, low redox potential, and faster electron–hole recombination render rutile ineffective.19 There has been immense interest to modify TiO₂ to enable it to absorb a wide range of wavelengths of solar energy,1,15,16 including the visible region.2,7,15,16,18 This has been achieved through various methods—metal20,21 or nonmetal doping,21,22 creating oxygen deficiency to form TiO₂−δ,23 dye sensitization15,16 or making TiO₂–quantum dots heterostructures.15,16,24 Factors such as the concentration and nature of the dopant, crystallite size, surface area, and anatase–rutile ratios2,4,6,14,19 control the photocatalytic efficiency of TiO₂.

Commercially available TiO₂ (Degussa P25) is a biphasic interfacial heterojunction of anatase–rutile (80:20).6,19,25 Bickley et al.25 were the first to propose a synergetic effect between anatase and rutile to be responsible for the relatively high photoreactivity of Degussa P25, in comparison to pure anatase or rutile.25 This is because the close proximity of anatase and rutile polymorphs results in two key processes:6,19,25–28 (1) the rutile phase with a lower band gap not only facilitates the production of charges in the visible light region but also transfers these charges to the conduction band of the anatase phase and eventually to the surface sites and (2) photogenerated holes from the valence band of anatase can be effectively transferred to that of rutile, thus leading to slow electron–hole recombination.6,26
anatase branched heterostructures were prepared by a combination of electrosprinning and the hydrothermal reaction.\textsuperscript{31} Patterned anatase–rutile junctions have been formed by calcination of patterned TiO\textsubscript{2} gel films.\textsuperscript{32} Pulsed-pressure MOCVD has been used to fabricate anatase–rutile heterojunctions.\textsuperscript{33} Porous films of TiO\textsubscript{2} mixtures have been prepared through plasma electrolytic oxidation (PEO).\textsuperscript{34} Heterogeneous nanostructures of anatase nanoparticles on rutile nanorods were synthesized through layer-by-layer, electrostatic deposition.\textsuperscript{34} Though the existing synthesis routes yield anatase–rutile mixtures/heterojunctions, in most cases, multistep reactions are involved and only a few of them yield porous products. While it is important to find simpler scalable methods for anatase–rutile mixtures of suitable ratios, it would also be of interest to obtain these in the form of light-weight porous monoliths so that these could be used as floats\textsuperscript{35} in water bodies for pollutant degradation applications. Our group has developed a self-sustained combustion synthesis of metal oxide foams using starch-based molded pellets.\textsuperscript{36,37} For example, t-ZrO\textsubscript{2} monolithic foams could be obtained by subjecting a pellet made up of ZrO(NO\textsubscript{3})\textsubscript{2}, urea, and starch.\textsuperscript{36,37} Adapting this method,\textsuperscript{36,37} in this work, we have synthesized macroporous monoliths of anatase–rutile TiO\textsubscript{2}. The excess of carbon in the reaction mixture ensured carbon doping (C-doping) of TiO\textsubscript{2}. These monoliths are found to be quite efficient in natural sunlight photocatalysis.

2. EXPERIMENTAL SECTION

2.1. Synthesis of Porous TiO\textsubscript{2} by the Combustion Method. Macroporous TiO\textsubscript{2} was prepared by the combustion method using TiCl\textsubscript{4} as a precursor, urea as a fuel, ammonium nitrate as an oxidizer and starch as a binder. Urea (0.011 mol, 0.7125 g) was mixed with 0.8435 g of ammonium nitrate (0.01 mol), starch, and 0.5 mL of TiCl\textsubscript{4} (0.86 g, 0.004 mol). The resulting mixture was ground into a dough-like consistency that could be molded into pellets of the desired shape. The mass of starch was varied from 100 to 2000 mg. The pellet was placed in a preheated crucible (800 °C) in an electric Bunsen. Instantly, a vigorous reaction was observed with the formation of an oxide foam. The oxide foam was heated in air at 800 °C for 20 min to burn away the organic remnants.

2.2. Photocatalytic Degradation of Dyes. Macroporous TiO\textsubscript{2} (10 mg) was dispersed in 100 mL of the dye solution (10 mg L\textsuperscript{-1}). The solution was stirred in the dark for 1 h. After attaining the equilibrium, the solution wasirradiated with natural sunlight. Aliquots were collected periodically, and the catalyst was removed by centrifugation. The dye concentration was monitored by measuring the absorbance of methylene blue (MB) at 664 nm and that of methyl orange (MO) at 464 nm.

2.3. Photocatalytic Selective Oxidation of Alcohol. Macroporous TiO\textsubscript{2} (10 mg) and 10 μL of benzyl alcohol (0.1 mmol) were added to 1.5 mL of oxygen saturated benzo trifluoride (BTF). The solution was stirred in the dark for 0.5 h. The solution was then transferred into a Pyrex glass filled with oxygen. The solution was irradiated with direct sunlight. After the reaction, the catalyst was removed by centrifugation. High-performance liquid chromatography (HPLC) was used to monitor the oxidation of the alcohol.

2.4. Characterization. The samples were characterized by X-ray diffraction (XRD) using a PANalytical Xpert pro diffractometer (Cu K\textalpha radiation, secondary graphite mono-chromator, scanning rate of 1° 2θ/min). IR spectroscopic studies were carried out in a PerkinElmer FTIR spectrophotometer (spectra two) in the range from 4000 to 550 cm\textsuperscript{-1} with a resolution of 4 cm\textsuperscript{-1}. X-ray photoelectron spectra (XPS) of the samples were recorded using a Kratos axis Ultra DLD. Scanning electron microscopy (SEM) images were recorded using a Zeiss, Ultra 55 field emission scanning electron microscope. A PerkinElmer LS 35 spectrometer was used to record the UV–visible spectra. The catalytic oxidation of benzyl alcohol was monitored by HPLC (Jasco) using a C18 column and a UV detector at 253 nm. A mixture of water and acetonitrile in a 70:30 volume ratio and 0.2 M phosphoric acid was used as the mobile phase. The mobile phase flow rate was maintained at 0.8 mL min\textsuperscript{-1}. The nitrogen sorption analysis was performed in a Belsorp mini-II instrument at liquid nitrogen temperature. The surface area of the material was determined by employing the Brunauer–Emmett–Teller equation. The pore sizes and pore volumes of the materials were obtained by the Barrett–Joyner–Halenda (BJH) method.

3. RESULTS AND DISCUSSION

The processes involved in the formation of porous TiO\textsubscript{2} monoliths by the starch pellet combustion method are schematically depicted in Figure 1. Once the combustion is initiated, the pellet catches fire and grows into a voluminous cylindrical foamy product, with its radius comparable to the radius of the initial pellet, within a few seconds. Partial burning of starch leaves behind a lot of carbonaceous impurities at this stage. Further heating in air burns away these impurities leaving behind a porous monolith of TiO\textsubscript{2}.

3.1. Catalyst Characterization. The XRD patterns of macroporous TiO\textsubscript{2} obtained by combustion synthesis with varying amounts of starch are shown in Figure 2. All of the peaks could be assigned to the anatase phase in the case of TiO\textsubscript{2} prepared in the presence of 100 mg of starch (Figure 2a). Peaks due to the rutile phase of TiO\textsubscript{2} are observed on increasing the mass of starch to 250 mg and above (Figure 2b–g). With an
The chemical composition of TiO₂ was further probed using X-ray photoelectron spectroscopy (XPS). The Ti 2p spectrum (Figure 3a) shows peaks (458.77 and 464.47 eV) due to Ti⁴⁺. The core-level C 1s spectrum (Figure 3b) exhibits peaks at 284.95, 286.47, and 288.86 eV that are ascribed to adventitious carbon from the internal standard, –C–O, and –C≡O, respectively. No peaks due to Ti–C (281 eV) were observed, indicating that carbon is not in the substitutional lattice position. These features suggest that carbon could be in the interstitial position of the TiO₂ lattice or as carbonate species at the surface. The infrared spectrum (Figure S2, Supporting Information) further corroborates the existence of –C–O species along with strong –O–H stretching and bending absorptions, indicating the interaction of moisture with surface carboxylate species. The N 1s spectrum (not shown) indicates the absence of nitrogen in the sample. These observations are in accordance with the literature for C-doped TiO₂.

The visible absorbance spectrum (Figure 3c) of porous TiO₂ (350 mg of starch) exhibits a broad absorption range in the visible region with a band gap of 2.51 eV calculated from the Tauc plot (the inset of Figure 3c). In comparison to theoretical 3.00 and 3.20 eV for rutile and anatase, respectively, narrowing of the band gap in porous TiO₂ is due to anatase–rutile heterojunctions in addition to contributions of dopants and defects as indicated by XPS studies. The SEM images (Figure 4a,b) of TiO₂ (350 mg of starch) show an irregularly shaped, coral-like, highly porous network with macropores of diameters of ~1 μm. The porous nature is further corroborated by the BET surface area measurements (Figure 4e,f). The surface area is measured to be 33.4 m² g⁻¹ with a pore volume of 0.12 cm³ g⁻¹ and a mean pore diameter of 14.6 nm, suggesting that TiO₂ obtained using 350 mg of starch exhibits macro- and mesopores. In comparison, the SEM image of TiO₂ (2000 mg of starch) comprises sheets (Figure 4c,d) that are in μm size laterally without any visible macropores. The surface area is measured to be 28.5 m² g⁻¹, with a pore volume of 0.009 cm³ g⁻¹ and a mean pore diameter of 14.0 nm, indicating that the material is mesoporous.

3.2. Mechanism of Formation of Anatase–Rutile Biphasic Porous TiO₂

The anatase–rutile transformation is reconstructive, wherein the transformation involves the breaking and reforming of bonds. As suggested in the previous studies, the amount of starch and ΔG°(f) of the metal oxide are expected to control the porosity of the material. The
amount of gases evolved depends on the mass of starch used. The energy released ($\Delta G^\circ$) during the reaction decides the local temperature. All of the reactions, using different amounts of starch, have been carried out under similar heating conditions. During combustion, the internal temperature is expected to increase when a higher mass of starch is being burnt, thus resulting in anatase–rutile transformation. However, experimental observations suggest that the internal temperature decreases with increasing amounts of starch.37 With a higher amount of starch, burning of starch through self-sustained combustion is slow, resulting in the lowering of the overall temperature. The reason for lower rutile content in the products seems to be purely kinetic. The total reaction time is $\sim 20$ min, which is insufficient to convert the initially formed anatase into rutile. The increased rutile content with an increase in starch may be attributed to the reductive atmosphere created by starch. During combustion, starch is dehydrated to give carbon, which being reductive in nature results in oxygen vacancies, leading to an increased rate of transformation of anatase to rutile.42

As the $\Delta G^\circ$ of TiO$_2$ is the same for reactions using 350 and 2000 mg of starch, the surface area and porosity solely depend on the nature of combustion of starch. With lower amounts of starch, the temperature is sufficient to cause high rates of the reaction, resulting in the local pressure build up and coral-like combusted products. As the starch content increases, the reaction proceeds at a lower rate, analogous to the smoldering of a cigarette stick.37 This is conducive to the formation of anisotropic products, as starch–sponge template could burn rapidly, uniformly leading to interconnected thin, porous sheets.

3.3. Photocatalytic Performance of Anatase–Rutile Biphasic Porous TiO$_2$ in Dye Degradation. The photocatalytic efficiency of porous TiO$_2$ prepared with varying amounts of starch was examined by monitoring the degradation of methylene blue under solar irradiation. The photocatalytic activity of porous TiO$_2$ summarized in Table 1 suggests that

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**Figure 4.** Bright-field SEM images of porous TiO$_2$ prepared using 350 mg of starch (a, b) and 2000 mg of starch (c, d). Nitrogen adsorption–desorption isotherms of porous TiO$_2$ prepared using 350 mg of starch (e) and 2000 mg of starch (f). The insets in (e, f) are the corresponding BJH plots.
TiO₂ prepared with lower starch content degrade the dye with minimum adsorption in comparison to TiO₂ prepared using a higher amount of starch. The UV−visible spectra of the dye extracted from the catalytic sample indicate that the reaction in the dark is adsorption and not degradation. The increased adsorption with the use of increased amounts of starch could be attributed to the increased surface −O−H and −C−O as the starch content increases, though the surface areas of all of the samples are comparable.

The photocatalytic activity of porous TiO₂ (350 mg of starch) in the degradation of MB and MO was evaluated under direct solar light. In all of the cases, prior to photocatalytic degradation, adsorption−desorption equilibriu m in the dark indicates negligible or low adsorption. Figure 5a,b represents the time-resolved UV−visible absorption spectra of photocatalytic degradation of MB and MO, respectively. In both cases, the intensity of the prominent absorption decreases with time. The log (absorbance) versus time plots (insets of Figure 5a,b) of MB and MO degradation indicate pseudo-first-order kinetics with rate constants of 0.034 and 0.0511 min⁻¹, respectively. Over four degradation cycles (the inset of Figure 5c), porous TiO₂ (prepared with 350 mg of starch) exhibits consistent catalytic activity. Adsorbed water and oxygen on the surface of TiO₂ produce reactive •OH and •O₂⁻ in the presence of sunlight. Degradation takes place only in the presence of a catalyst and sunlight (Table S1, Supporting Information) due to the increased concentration of net oxidizing species in solution. Nonlinear dependency on the amount of the catalyst appears to be exponential with saturation beginning at 10 mg of the catalyst (Figure 5c).

One of the requisites of an ideal catalyst is its ability to catalyze the degradation of organics under all pH conditions. The effect of pH on the degradation of MB (Figure 5d) clearly indicates that porous TiO₂ effectively catalyze dye degradation in a wide range of pH values.

Table 1. Summary of the Solar Photocatalytic Degradation of Methylene Blue (100 mL, 10 ppm) using 10 mg of Porous TiO₂ Synthesized using Varying Amounts of Starch

| starch (mg) | % composition | adsorption (%) | MB degradation | time (min) |
|------------|---------------|---------------|----------------|------------|
| 100        | 100 anatase    | 0             | 0              | 120        |
| 250        | 96 anatase, 4 rutile | 4             | 80             | 120        |
| 350        | 85 anatase, 15 rutile | 6             | 100            | 80         |
| 500        | 82 anatase, 18 rutile | 12            | 100            | 110        |
| 750        | 70 anatase, 30 rutile | 19            | 100            | 120        |
| 1000       | 67 anatase, 33 rutile | 30            | 100            | 120        |
| 2000       | 60 anatase, 40 rutile | 42            | 100            | 120        |

Figure 5. Degradation of dyes (10 mg L⁻¹) was traced through UV−visible absorption spectra of reaction mixtures containing 10 mg of porous TiO₂ heterojunctions as a photocatalyst. Evolution of absorption spectra with time in the case of (a) MB and (b) MO, and the insets correspond to log (absorbance) versus time plots. Variation of the photocatalytic MB (100 mL, 10 mg L⁻¹) degradation efficiency with (c) mass of porous TiO₂ heterojunctions as a catalyst and (d) pH. Catalytic efficiency over repeated cycles in the case of MB degradation is shown as the inset in (c).
follows (Figure 6B). The conversion and selectivity were de-
conversion of 80% with 100% selectivity was achieved in 60 min
of the acid being zero at all times, indicating 100% selectivity. A
increase in the concentration of aldehyde with the concentration
decrease in the concentration of alcohol and a corresponding
alcohol.11,43
potential photocatalyst in selective oxidation of benzyl
molecules by optically excited TiO2 is thermodynamically
feasible at room temperature in the presence of oxygen.11 The
photogenerated holes with an oxidation potential of 3.0 V
renders TiO2 with considerable oxidizing capability.11,43
Benzaldehyde is a widely used raw material in pharmaceutical
industries. Benzaldehyde is synthesized through selective
oxidation of benzyl alcohol using liquid-phase chlorination, a
toxic and corrosive process.11,44 It is of importance to develop
alternative chlorine-free routes to produce benzaldehyde.44,45 In
the presence of noble metal46 or transition metal complexes47 as
catalysts, molecular oxygen has emerged as a primary oxidant in
the oxidation of alcohols to carbonyl compounds.11,44 In
Photocatalytic selective organic transformations,44–47 utilizing
renewable solar energy, have garnered interest as a greener and
efficient route.44–46 Environmentally benign, economically
viable, and naturally abundant TiO2 has been explored as a
potential photocatalyst in selective oxidation of benzyl
alcohol.11,43–47
Benzy alcohol interacts with the surface hydroxyl groups of
the photoexcited porous TiO2. The photogenerated holes in
TiO2 abstract the protons from benzyl alcohol, while the alcohol
loses an electron and gets oxidized to aldehyde. The longer
surface adsorption of the reactant (alcohol) or the product
(aldehyde) not only leads to a decrease in the photocatalytic
activity of TiO2 but also leads to further oxidation of aldehyde to
carboxylic acid, thus minimizing the selectivity of the oxidation process.
The porous TiO2 (prepared using 350 mg of starch)
heterostructure exhibits excellent photocatalytic activity toward
selective oxidation of benzyl alcohol to benzaldehyde. The
HPLC chromatograms of the aliquots of the reaction mixture
taken at different time intervals (Figure 6A) show a gradual
decrease in the concentration of alcohol and a corresponding
increase in the concentration of aldehyde with the concentration
of the acid being zero at all times, indicating 100% selectivity. A
conversion of 80% with 100% selectivity was achieved in 60 min
(Figure 6B). The conversion and selectivity are defined as follows
conversion percentage = (Co – Calk) / Co × 100

\[ \text{selectivity percentage} = \frac{C_{\text{aldehyde}}}{(C_o - C_{\text{alcohol}})} \times 100 \]

C0 is the initial concentration of benzyl alcohol, Calk and
Caldehyde are the concentrations of benzyl alcohol and
benzaldehyde, respectively, at a given reaction time. However,
beyond 60 min, the progress of the reaction was quite slow and a
conversion percentage of 87 was observed after 120 min. The
catalyst could be recovered and reused to get similar results over
four cycles.

3.5. Reasons for the Enhanced Photocatalytic Per-
formance of Anatase–Rutile Biphasic Porous TiO2.
Adsorbed water and oxygen on the surface of porous TiO2
monoliths produce reactive *OH and *O2•− in the presence of
sunlight. These radicals cause degradation of the dye. The
porous monolith architecture of TiO2 facilitates the formation of
more heterojunctions, thereby increasing the activity. With the
conduction band edge of rutile ~0.2 eV lower than that of
anatase, the photoexcited electrons are effectively transferred
from the conduction band of rutile to that of anatase at the
interface between anatase and rutile.5,26 While this promotes
photoreduction at the anatase site (Figure 7), photooxidation
takes place either on the anatase or rutile surface.

Figure 7. Schematic of the processes involved in the sunlight
photocatalytic activity of porous biphasic C-doped TiO2 monoliths.

The photocatalytic performance of all of the porous TiO2
monoliths is higher than that of commercial Degussa P25. This
is attributed to the following reasons: (1) a porous network
provides channels for faster reactant diffusion and more active
catalytic sites, (2) anatase–rutile heterojunctions aid in
electron–hole separation and a wider range of solar energy
absorption, and (3) doped carbon not only contributes to the
lowering of the absorption band gap of TiO$_2$ but also renders the TiO$_2$ surface hydrophilic due to increased interaction with moisture through hydrogen bonding. The heterojunctions obtained using 350 mg of starch exhibit higher photocatalytic activity in comparison to all other TiO$_2$ monoliths (Table 2). The highest activity could be as a result of optimum anatase−rutile composition (85:15) and the presence of interstitial carbon as −C=O that aids in better wettability of the catalyst and thus faster interaction and degradation of organics.6,38,41 TiO$_2$ prepared using 100 and 200 mg of starch exhibit lower photoactivity (Table 1) due to the low percentage of anatase−rutile heterojunctions (Figure 2). On the other hand, increasing the percentage of anatase−rutile heterojunctions and carbon doping using higher starch content (Table 1) also does not improve the performance of porous TiO$_2$. Further, the surface areas of TiO$_2$ prepared using 350 and 2000 mg of starch are comparable. Therefore, the increased solar photocatalytic activity for the heterojunctions can be correlated to the combined effect of the porous network, band gap narrowing due anatase−rutile heterojunctions, and carbon doping. Porous TiO$_2$ prepared using 350 mg of starch shows better performance in dye degradation under solar light compared to the already known TiO$_2$-based catalysts (Table 2). In fact, its catalytic activity under sunlight is better than some of the catalysts under UV irradiation. For selective oxidation of benzaldehyde, our catalyst under sunlight performs better than known catalysts under UV light. The enhanced photocatalytic activity under ambient conditions in natural sunlight renders porous TiO$_2$ monoliths a superior catalyst and a desired material for environmental amelioration.

### Table 2. Comparison of Photocatalytic Activities of Porous TiO$_2$ (350 mg of Starch) with other TiO$_2$ Catalysts Reported in the Literature

| catalyst | BET surface area (m$^2$ g$^{-1}$) | mass of the catalyst (mg) | pollutant conc. in ppm and (volume) | degradation | irradiation source | time (min) | % ref |
|----------|---------------------------------|--------------------------|-----------------------------------|-------------|-------------------|------------|-------|
| Methylene Blue Degradation | | | | | | | |
| porous TiO$_2$ (A/R = 85:15) | 33.37 | 10 | 10 (100 mL) | sunlight | 80 | 100 | present work |
| TiO$_2$ nanoflower (A/R = 99:1) | 36.9 | 30 | 12.79 (150 mL) | UV light | 30 | 100 | 17 |
| TiO$_2$ A/B nanoparticles | 183.6 | 60 | 10 (600 mL) | UV light | 180 | 97 | 48 |
| TiO$_2$ rods (A = 100%) | 40.5 | 30 | 12.79 (150 mL) | UV light | 40 | 80 | 49 |
| mesoporous TiO$_2$ (A/B = 80:20) | 186 | 120 | 32 (200 mL) | UV light | 70 | 100 | 50 |
| TiO$_2$ anatase/rutile nanoflowers | 106.29 | 10 | 15 (20 mL) | 350 W xenon lamp | 120 | 72 | 51 |
| graphene-wrapped anatase−rutile hierarchical TiO$_2$ nanoflower | 33.2 | 30 | 500 (40 mL) | 500 W Hg lamp | 30 | 100 | 52 |
| porous TiO$_2$ (A/R = 55:45) | – | – | 1.28 (30 mL) | UV light | 100 | 100 | 33 |
| TiO$_2$−N$_2$ heterojunction (A/R = 90:10) | 79.6 | 60 | 3 (50 mL) | solar simulator | 180 | 90 | 19 |
| TiO$_2$ (A = 100%) | 159 | 1.6 | 10 (8 mL) | UV light | 180 | 90 | 53 |
| nanocrystalline TiO$_2$(A = 100) | 246 | 100 | 100 (100 mL) | sunlight | 225 | 100 | 38 |
| TiO$_2$ (A = 100) | 29 | 20 | 10 (40 mL) | UV light | 180 | 100 | 18 |
| TiO$_2$ nanofilms (A = 100%) | – | 100 | 4 (100 mL) | UV light | 50 | 67 | 54 |
| Methyl Orange Degradation | | | | | | | |
| porous TiO$_2$ (A/R = 85:15) | 33.37 | 10 | 10 (100 mL) | sunlight | 105 | 91 | present work |
| core−shell rutile−anatase TiO$_2$ | – | 20 | 10 (150 mL) | UV light | 150 | 100 | 55 |
| porous TiO$_2$−Pt−rGO | 61.7 | 20 | 10 (20 mL) | 300 W xenon lamp | 120 | 80 | 56 |
| TiO$_2$ nanoflower (A/R = 82:18) | 165 | 300 | 10 (300 mL) | 500 W xenon lamp | 60 | 98 | 57 |
| Benzyl Alcohol Oxidation | | | | | | | |
| catalyst | BET surface area (m$^2$ g$^{-1}$) | mass of the catalyst (mg) | conc. of alcohol (mmol) | dehydration | irradiation source | time (min) | % conversion; selectivity | ref |
|porous TiO$_2$ (A/R = 85:15) | 33.37 | 10 | 0.1 | sunlight | 60 | 80; 100 | present work |
| CdS/TiO$_2$ | 201 | 8 | 0.1 | 500 W xenon lamp | 240 | 45; 97 | 8 |
| carbonate like doped TiO$_2$ | 160 | 16 | 0.1 | 300 W xenon lamp | 360 | 80.6; 99 | 58 |
| TiO$_2$−CdS QDs | 144 | 50 | 0.2 | 300 W xenon lamp | 180 | 95; 100 | 9 |
| CdS/TiO$_2$ composites | 42.9 | 8 | 0.1 | 300 W xenon lamp | 240 | 22.3; 100 | 10 |
| TiO$_2$ (A = 100%) | 210 | 53 | 0.1 | 100 W Hg lamp | 240 | 51; 99 | 11 |

$^a$A = anatase; R = rutile; and B = brookite.

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Solar light active macroporous C-doped TiO₂ heterojunction photocatalysts were prepared through simple, single-step, self-sustained combustion reactions. Porous monoliths of different anatase–rutile ratios (increasing rutile component from 0 to 40%) were obtained by varying the amount of starch. Monoliths with an anatase–rutile ratio of 85:15 exhibit exceptional photocatalytic activity in the degradation of dyes (methylene blue and methyl orange) and selective oxidation of benzyl alcohol to benzaldehyde under natural sunlight. The synthesis route could be used as a general strategy to synthesize economically viable TiO₂ monoliths with multiple features for efficient natural sunlight photocatalytic applications such as H₂ production and CO₂ conversion.

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**Notes**

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