Tailored synthesis of anatase-brookite heterojunction photocatalysts for degradation of cylindrospermopsin under UV-Vis light

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Abstract

Anatase-brookite heterojunction TiO₂ (ABH) photocatalysts were purposefully tailored by introducing different glycine concentrations through hydrothermal treatment at 200 °C for 20 h. In the absence of glycine, pure anatase and brookite phases were selectively prepared via simply adjusting the initial pH value with NH₄OH or NaOH. The as-synthesized photocatalysts were characterized with X-ray diffraction (XRD), Raman spectroscopy, UV-Vis diffuse reflectance spectra (DRS), photoluminescence (PL), surface area measurements, Fourier transform infrared spectroscopy (FT-IR) and field emission-scanning electron microscopy (FE-SEM). The XRD revealed that brookite content decreased in ABH samples with glycine concentration increased. The prepared TiO₂ nanoparticles have mesostructure with large surface area values ranging from 27.9 to 62.3 m² g⁻¹. SEM images showed spindle-like brookite structure and rod-like brookite mixed with small anatase particle obtained in the absence and presence of glycine, respectively. The electron-hole recombination efficiency in ABH photocatalysts was much lower than that in single phase

TiO₂. The absorption edges of ABH samples were red-shifted in the range of 250-400 nm. The activities of as-prepared TiO₂ photocatalysts were evaluated for the degradation of cylindrospermopsin(CYN) under UV-Vis light. Complete CYN degradation (100%) from aqueous solution with initial rate of $175 \times 10^{-3} \mu\text{M min}^{-1}$ was achieved under UV-Vis light irradiation within 15 min. This was attributed to its unique crystal phase composition, mesoporous structure and high surface area.

Keywords:Anatase; Brookite; Heterojunction; Photocatalytic; Degradation; Cyanotoxins

1. Introduction

Cylindrospermopsin (CYN) is a natural toxin produced by several fresh water cyanobacteria species [1]. CYN contains a tricyclic guanidine unit and hydroxy methyl uracil moiety and is highly soluble in water [2]. CYN has harmful impacts on human health and specifically can exhibit neurotoxic, hepatotoxic, carcinogenic, genotoxic, and cytotoxic effects [1,2]. CYN was first discovered after the 1979 Palm Island mystery disease in Queensland, Australia [1,3,4]. The need of controlling the occurrence of CYN in water and examine more its human and environmental effects are among the reasons for intense research on this toxin and its recent inclusion by the U.S. Environmental Protection Agency (EPA) on their Contaminant Candidate List (CCL) IV [5]. More recently (May 2015), U.S. EPA has set a 10-day advisory for CYN of 0.7 mg L^{-1} for children under 6 years old and 3.0 mg L^{-1} for adults [6]. In the last decade, CYN contamination in several aquatic systems around the world has drawn concerns by people and has spurred scientific attention by scientists and water treatment professionals towards the development of efficient treatment and monitoring technologies for this toxin.

So far, the conventional technologies such as coagulation, flocculation and filtration as well as activated carbon via physical adsorption, are considered inefficient for the removal of CYN from water at low concentrations [1-4]. Advanced oxidation processes (AOPs) are considered promising technologies for CYN removal, as AOPs are based on the generation of highly reactive hydroxyl

radical ($\cdot\text{OH}$) which possess high oxidation potential (+2.80 V) [7]. TiO_2/UV photocatalysis is a promising process for the destruction and detoxification of CYN in water due to the effectiveness of this catalyst to degrade toxin and the possibilities to use the UV component of the solar light [8]. Unfortunately, the undesired electron–hole recombination of TiO_2 nanopowders results in low photonic efficiency for the TiO_2/UV photocatalytic process [9]. Mixed TiO_2 phases have been reported to exhibit increase in the separation of the electron–hole pair thus, reduced recombination. In turn, this leads to a synergistic effect between different TiO_2 phases and a consequent enhancement of photocatalytic activity [7,10-12]. Recently, the synthesis of mixed TiO_2 phases such as anatase/rutile, anatase/brookite, brookite/rutile and anatase/brookite/rutile have been reported; however, the ability to control the crystal phase of TiO_2 is still difficult in identifying suitable preparation process [1,10-12]. Therefore, it is of great importance to develop an effective method to synthesize mixed-phase TiO_2 with tunable ratios of two phases. To the authors' knowledge, only a few reports have so far been published focusing on the synthesis of TiO_2 with controllable phases of anatase and brookite [10-12]. Moreover, TiCl_4 or titanium alkoxide precursors were usually used in the previously published synthesis methods and these materials are very sensitive to moisture and should, hence, be handled under inert gas and/or the processes suffer from multi steps which might lead to low yields. Kandiel et al. [12] used titanium bis(ammonium lactate) dihydroxide (TALH) and urea to synthesize TiO_2 polymorphs with a tunable anatase/brookite ratio. The ratios of anatase to brookite in mixed-phase TiO_2 nanocrystals could be easily tuned by simply altering the additional amount of urea. The applied titanium source (TALH) is too expensive for large scale application and large amounts of ammonia would be released before or after the reactions, which are harmful to the environment.

Recently, glycine as α -aminocarboxylic functional group was used for the synthesis of anatase/brookite TiO_2 [13,14]. Tao et al. used tetra-n-butyl titanate (TBT), sodium hydroxide (NaOH) and glycine to prepare mainly anatase nanoflower. They used different amounts of glycine to follow up the flower morphology not the phase composition of TiO_2 . They prepared one sample of

anatase/brookite TiO_2 with low crystallinity; however they did not study its performance in the photocatalytic reactions[13].

Cihlar et al. [14] used titanium isopropoxide (TTIP) and nine kinds of chelate-forming substances including glycine for a synthesis of titanium dioxide via sol-gel complex synthesis. By using glycine, they obtained ABH samples without tailoring via solid state reaction and by changing the sol-gel reaction temperature from 80 to 100 °C. The resulting morphology was nanoparticles with phase composition 87-79 % A/ 13-21% B.

Only a limited number of studies have been focused on the degradation of CYN via TiO_2 /UV-Vis photocatalysis. For example, Zhang et al. [1] used titanium tetrachloride (TiCl_4) as titanium source to synthesize anatase–brookite–rutile polymorphic TiO_2 (PM- TiO_2) via a sol–gel process using a low temperature oil bath for the removal of CYN from water under UV-Vis light. Furthermore, the influences of PM- TiO_2 loading (0.05–0.50 g L⁻¹), pH (4.0, 7.5 and 10.5), and addition of natural organic matter (NOM)) were examined and discussed. They found that the optimum photocatalyst loading is 0.25 g L⁻¹, optimum pH is 4.0 and the radical scavenging effect of NOM retards the reaction rate. Chen et al. [8] used titanium dioxide powder (Degussa P-25) for degradation and detoxification of CYN from aqueous solution under UV light. They reported detailed product studies during the rapid degradation and detoxification of CYN. They demonstrated that UV TiO_2 photocatalysis has promise as an efficient treatment method for oxidative degradation and detoxification of CYN and other cyanotoxins. To the best of the authors' knowledge, the degradation of CYN using ABH TiO_2 has not been reported up to date. Therefore, a great challenge remains to synthesize A/B mixed-phase TiO_2 with tunable ratios of the two phases using low-cost and non-toxic precursors and its application for the degradation of CYN under UV light.

In this work, for the first time, the synthesis of high quality brookite nanospindles is reported with the advantage of tailoring A/B ratio by a facile hydrothermal method using aqueous solutions of commercially available titanium (III) sulfate ($\text{Ti}_2(\text{SO}_4)_3$) in the presence of glycine. Titanium (III)

sulfate was chosen as the titanium source, because it is easily manipulated, and glycine was also chosen as the typical α -aminocarboxylic acid for tailoring A/B ratio, as it is of low-cost and non-toxic. The ratios of anatase to brookite in ABH TiO₂ nanocrystals could be easily tuned by simply changing the additional amount of glycine. Moreover, pure anatase was prepared in the absence of glycine at pH 10 adjusted via NH₄OH. The physicochemical properties and morphology of the as-prepared catalysts (A-TiO₂, B-TiO₂ and ABH-TiO₂) were determined using various advanced techniques and their photocatalytic activities were compared based on the degradation kinetics of CYN under UV-Vis light. The results revealed rapid and complete CYN degradation from aqueous solution with fastest initial degradation rate ($175 \times 10^{-3} \mu\text{M min}^{-1}$) under UV-Vis irradiation from the TiO₂ sample with (61.8% A and 38.2% B) h2 sample.

2. Experimental details

2.1. Synthesis of TiO₂ powders

The oxidizing agent, NaNO₃ (98%, Koch-light laboratories Ltd UK) was added to Ti₂(SO₄)₃ (15%, aqueous solution, Fisher) followed by stirring until the formation of a colorless and transparent solution (pH was about 3). The NH₄OH (25%, Sigma-Aldrich) or NaOH (98%, Pellets, LobaChemie) were introduced into the colorless solution until pH 10 was reached to synthesize pure anatase or brookite, respectively. The synthesized anatase-brookite heterojunction TiO₂ catalysts were obtained by adjusting the pH value of the colorless solution to 10 with NaOH in the presence of different amounts of glycine (99%, Sigma-Aldrich). The 75 ml of the resulting solution was placed into 100 ml Teflon-lined stainless-steel autoclave and heated at 200 °C for 20 h, then left to cool. The obtained solid was centrifuged and washed several times with water and ethanol, and then dried at 60 °C for 12 h. The synthesis process was based on the work of Shen et al. [\[10,11\]](#).

2.2. Catalyst characterization

The crystal structure, relative crystallinity and crystal size of the samples were characterized by X-ray diffraction (XRD, Brukeraxs D8, Germany) using Cu K α radiation ($\lambda = 0.15405$ nm) and a secondary monochromator in the 2θ range from 20 to 70°. Relative crystallinity was calculated from the area under the most intense peak of XRD patterns. Crystallite size was determined from the XRD results using the Debye-Scherrer equation. Raman analysis was performed on a Senterra Dispersive Micro Raman (Bruker, Germany) utilizing a doubled Nd:YAG laser ($\lambda = 532$ nm) 10 mW as the excitation source. The BET specific surface area, pore volume, and pore size distribution measurements of the samples were determined by the N₂ adsorption–desorption method at 77 K (Nova 2000 series, Quantachrome Instruments, UK), after being degassed at 453 K for overnight. PL analysis was carried out using a spectrofluorophotometer (Shimadzu RF-5301PC) at 25 °C with an excitation wavelength of 300 nm. The optical characteristics and band gap of the samples were obtained by applying UV spectrophotometer (UV-2501 PC, Shimadzu) with an integrating sphere attachment (ISR 1200) for diffuse reflectance measurement and BaSO₄ powder was employed as the diffuse reflectance standard. The reflectance data were transferred into the sphere's diffuse accessory and using absorption coefficient F(R) values according to the modified Kubelka-Munk function. The FT-IR spectra were examined at 25 °C with samples in a KBr wafer (JASCO 3600). The crystal shapes of the obtained catalysts were characterized using a field emission-scanning electron microscope (FE-SEM, QUANTAFEG 250, Netherlands).

2.3. Photocatalytic activities

For all experiments, aqueous suspension of TiO₂ photocatalysts (0.25 g L⁻¹) was prepared with ultrasonication mixing (frequency of 40 kHz) in a cleaning bath for 20 min. and Room temperature (23 °C). The photocatalytic experiments were carried out in a sealed round Petri dish reactor (Pyrex, 60 mm (ϕ) $\times$ 15 mm (h)) and irradiated by two fluorescent lamps (Cole-Parmer, 15 W, wavelength range 310 to 720 nm) with continuous stirring and temperature control at a neutral pH. To avoid temperature increase due to radiation, the photocatalytic reactor cell was under air circulation using a fan. A radiant power meter (Newport Corp) was used to measure the radiation intensity (2.37 mW

cm⁻²). Solid CYN (EMD Biosciences) was used without further purification with the initial concentration of 1 μ M in all experiments. Through the photocatalytic experiment, 200 μ L samples were taken at predetermined time intervals, diluted with 200 μ L reaction solvent matrix, and then filtered via syringeless filter (0.2 μ m, PTFE, Whatman) to remove the solid TiO₂ prior to quantification of CYN concentration. The concentration of CYN was quantified with high-performance liquid chromatography (HPLC, Series 1100, Agilent) with a photodiode-array detector (PDA) set at 262 nm. A C18Discovery HS (Supelco) column (150 mm $\times$ 2.1 mm, 5 μ m particle size) was employed as the stationary phase, while the mobile phase was 0.05% (v/v) tri-fluoroacetic acid (TFA, 101.7%, Fisher) in Milli-Q water. The analysis was performed under equilibrium conditions with a column temperature of 40°C, a flow rate of 0.3 mL min⁻¹ and an injection volume of 50 μ L[1].

3. Results and discussion

3.1. Physical and chemical characterization of as-prepared catalysts

Five samples were prepared under different reaction conditions and are denoted as h1, h2, h3, h4, and h5. The crystallographic structures of the samples characterized by powder XRD patterns are depicted in Fig. 1(A). The diffractions can be indexed to anatase (JCPDS 84-1286) and brookite phases (JCPDS 15-0875). Clearly, it indicates two possibilities: the first one is the formation of pure brookite (B-TiO₂) and anatase (A-TiO₂) in the absence of glycine; and the second one is the formation of anatase/brookite heterojunction TiO₂ (ABH) in the presence of glycine. The h1 and h5 samples, for which no glycine is added, are composed of pure anatase and brookite, respectively. The existence of brookite with orthorhombic crystal structure in the h5 sample can be readily discerned from its (121) crystallographic plane, located at ($2\theta \cong 30.8^\circ$) in the XRD pattern. To claim pure brookite phase, attention should be paid to the reflection of brookite (121) and the reflection of anatase (120) in which overlapping with brookite reflection can occur. The XRD peaks of brookite and anatase have an approximate ratio of 0.9, revealing the high purity of the as-

prepared brookite, which is consistent with previous literature studies [10-12]. On the other hand, when the glycine was introduced into the reaction system, ABH (i.e. h2, h3 and h4 samples) materials were obtained. The phase compositions of all samples can be estimated from the integral intensities of the anatase (101) and brookite (121) reflections using the equation reported by Zhang and Banfield, with optimized coefficients K_A and K_B as 0.886 and 2.217, respectively [15]. The crystal size of each phase was calculated by applying the Scherrer formula [16]. It was clear that pH, Na^+ , NH_4^+ , OH^- and glycine have been played critical roles in determining the crystal structure and phase content of the as-prepared TiO_2 samples. Firstly, in the absence of glycine at pH10 with NaOH (2M) and NH_4OH (25%), 100 % brookite and 100 % anatase were obtained, respectively. Then, in the presence of glycine at pH10 with NaOH (2M), ABH samples were obtained. It was observed that brookite/anatase ratio in ABH samples decreased with increase in glycine concentration to be in the following order: $h2 < h3 < h4$. The reaction condition, phase percentages and crystal size of the obtained TiO_2 samples are listed in Table 1. The relationship between phase content and glycine concentration is shown in Fig. 1(B).

The purity and crystal structure of obtained catalysts were further confirmed using Raman spectroscopy in the range of 100 to 700 cm^{-1} , as displayed in Fig. 2. The Raman spectrum of h1 sample shows Raman active modes of anatase phase [17], whereas the Raman spectrum of h5 sample shows rich characteristic signals of brookite [18]. On the other hand, the Raman peaks of bi-phase anatase and brookite mixture are presented in h2, h3 and h4 samples [17,18]. In the heterojunction catalysts (h2, h3 and h4 samples), as the glycine concentration increases, the Raman peak position slightly increases, which is attributed to increasing anatase and thus decreasing brookite content in heterojunction samples [12]. The Raman data obtained are illustrated in Table 2.

Fig. 3 presents the FT-IR spectra of as-prepared TiO_2 catalysts in the range of 4000-400 cm^{-1} . The absorption broad bands located around 3600-3000 cm^{-1} and the sharp band at 1630 cm^{-1} are related to bending and stretching vibrations of hydroxyl group (O-H) of surface adsorbed water molecules, respectively [1,19]. Moreover, the stretching modes of OH groups can be assigned to non-free

water (coordinated water molecules), whereas, the binding modes of OH groups can be ascribed to free surface adsorbed water [19]. It was observed that the broadband of brookite TiO_2 is located at 3421 cm^{-1} . This broad band is red-shifted in ABH- TiO_2 samples, and as anatase content increases in these samples, the broadband position is gradually red-shifted from 3410 to 3525 cm^{-1} . The known low energy IR bands around $900\text{--}400\text{ cm}^{-1}$ are characteristic for the stretching vibrations of Ti–O and Ti–O–Ti bonds in TiO_2 samples [2,19].

The surface area of the samples was measured using the BET method. The results illustrate the surface area is greatly dependent on phase structure and composition, where the measured surface areas of ABH- TiO_2 ($34\text{--}62.3\text{ m}^2\text{g}^{-1}$) samples are higher than that of anatase ($32.3\text{ m}^2\text{g}^{-1}$) and brookite ($27.9\text{ m}^2\text{g}^{-1}$) phase TiO_2 . The surface area increases with increasing the content of anatase in the ABH- TiO_2 samples, as summarized in Table 1. The nitrogen adsorption–desorption isotherms of the TiO_2 powders are presented in Fig. 4. The data indicates that all samples displayed a type IV isotherm according to IUPAC classification [20–22]. According to the Barrett-Joyner-Halenda (BJH) pore-size distribution of the TiO_2 powders, pore sizes of 24.5 and 34.5 nm were estimated for the mesoporous structures for samples h1 and h2, respectively. Furthermore, the micropore sizes were estimated to be 0.467 , 1.117 , and 1.476 nm for samples h3, h4 and h5, respectively, as listed Table 1.

The photoluminescence spectra (PL) analysis is a suitable good tool to indicate the fate of e^-/h^+ pairs in titania lattice [23]. Fig. 5 displays PL spectra of the samples excited at $\lambda = 300\text{ nm}$ at 25°C , in the range of $350\text{--}600\text{ nm}$. The data indicate that PL spectra peaks of all samples are located at the same position around 470 nm , which can be assigned to the recombination of self-trapped excitation luminescence [24]. PL intensity of the samples is in the following sequence: $h5 > h1 > h4 > h3 > h2$, as shown in Fig. 5. Hence, life time separation of photo-generated e^-/h^+ pairs is in the following order: $h2 > h3 > h4 > h1 > h5$. Normally, as the content of anatase increases in the ABH- TiO_2 samples, the intensity of the PL spectra decreases.

The UV-Vis diffusion reflectance spectra of yielded TiO₂ are shown in Fig. 6. The significant increase of the absorption in the UV irradiation range can be related to the band-gap absorption of TiO₂. As shown in Fig. 6(A), the light absorption of B-TiO₂ and A-TiO₂ are obviously lower than that of bi-phase anatase/brookite mixture in the range between 250 and 400 nm. As brookite content increases in the ABH-TiO₂ powders, the absorption edge gradually decreases from 399 to 379.4 nm, so the band gap values of TiO₂ obtained are increased. TiO₂ is known as an indirect semiconductor [25] and the effective band gap (E_g) can be estimated by the Kubelka–Munk function by plotting $((F(R).hv)^{1/2})$ vs the photon energy. In addition, the linear segment of the spectra is extrapolated to intersect the photon energy axis to obtain the indirect band gap (E_g) value of the measured sample [26]. The Kubelka–Munk equation is used to convert the reflectance to absorption coefficient F(R) [27]. The modified Kubelka–Munk function is shown in Eq. (1) below:

$$F(R) = \frac{(1 - R)^2}{2R} \quad (1)$$

Where R is the proportion of light reflected. The effective band gaps of the h1, h2, h3, h4 and h5 TiO₂ samples are 3.17, 3.19, 3.2 and 3.26 eV, respectively, as shown in Fig. 6(B), and Table 1. The band gap increasing in value subsequently with increasing brookite content and this is due to the quantum-sized effect [28]. The band gap energy values are in agreement with the photocatalytic activity of TiO₂ samples where the brookite TiO₂ of the highest band gap energy among the samples has the lowest photocatalytic activity and this is in agreement with literature data [29].

The morphologies of three samples were estimated by field emission-scanning electron microscopy, as shown in Fig. 7. It is indicated that addition of NaOH, NH₄OH, and glycine through TiO₂ preparation plays a crucial role in the TiO₂ phase transformation, particles size, and shape of the obtained TiO₂ samples. Fig. 7(A) shows that h1 sample, obtained at glycine-free and pH10, adjusted by NaOH, shows small particle size, suggesting presence of anatase phase which was confirmed by XRD analysis. On the other hand, pure brookite obtained at glycine-free and pH 10, adjusted by NH₄OH, is composed of spindle-like structures with diameter up to 25 nm and lengths up to 108 nm

[10,18], as shown in Fig. 7(B). The brookite spindle-like morphology in the SEM micrograph reveals a high uniformity and a clean surface without any contamination. The micrograph of h2 sample is shown in Fig. 7(C). The data indicate that the morphology of sample h2 consists mainly of rod-like particles, accompanied by some small particles and the spindle-like structures disappeared. From the XRD patterns, we can conclude that the small particles are assigned to the anatase phase and the rod-like particles are ascribed to brookite phase.

A formation mechanism, shown in scheme 2, has been proposed based on our experimental results, which reveal the essential role of pH value, Na^+ , NH_4^+ , OH^- and glycine for the transformation from a layered titanate structure to pure brookite or pure anatase even or ABH under hydrothermal treatment. Firstly, titanium (III) sulfate was oxidized by NaNO_3 to facilitate the formation of insoluble $\text{Ti}(\text{OH})_4$ after direct hydrolysis. $\text{Ti}(\text{OH})_4$ has been transformed into a layered titanate under hydrothermal treatment [10]. Sodium ion (Na^+) plays a key role in the formation of brookite TiO_2 [11], where in the absence of glycine, by adding NaOH (2M) to adjust the pH at 10, amorphous sodium titanate ($\text{Na}_{2-x}\text{H}_2\text{Ti}_2\text{O}_5 \cdot \text{H}_2\text{O}$) is formed due to the strong electrostatic interaction between Na^+ cations and TiO_6 units of the layered titanate [11,30]. Finally, the electrostatic interaction in sodium titanate decreases internal structural tension as Na^+ or H^+ ions can be progressively liberated [30,31]. Hence, the layered structure becomes unstable and ultimately transforms into brookite as the dominant crystalline phase with a major Miller index (121) located at $2\theta = 30.8^\circ$ at pH 10, which is consistent with the literature [30]. However, when adding NH_4OH to adjust the pH, NH_4^+ ions exist in the interlayer of titanate to balance the negative charges of the layered titanate to form ammonium titanate ($(\text{NH}_4)_{2-x}\text{H}_2\text{Ti}_2\text{O}_5 \cdot \text{H}_2\text{O}$) [11]. Ammonium ion is then eliminated thermally with heating at 200°C [11]. Ultimately, the proton ions from NH_4^+ ions induce hydroxyl condensation reaction to form anatase phase with a major Miller index (101) at $2\theta = 25.3^\circ$ [11]. On the other hand, ABH samples have been obtained by adding glycine ($\text{C}_2\text{H}_5\text{NO}_2$) at pH 10 adjusted by NaOH . The soluble and insoluble Ti-contained species have been formed with adding glycine into the reaction system [10], where under hydrothermal treatment, the insoluble amorphous $\text{Ti}(\text{OH})_4$ could first

transform to layered titanate ($\text{Na}_{2-x}\text{H}_2\text{Ti}_2\text{O}_5 \cdot \text{H}_2\text{O}$). However due to large steric hindrance of glycine chelate with Ti center, the soluble five-membered ring complexes $[\text{Ti}(\text{OH})_x(\text{C}_2\text{H}_5\text{NO}_2)_y]^z$ combine together by sharing equatorial edges and get arranged in zigzag chains, which benefited the formation of anatase crystallites [10]. As glycine concentration increase, five-membered ring complexes increase in expense of amorphous $\text{Ti}(\text{OH})_4$, therefore, A/B ratio in the ABH samples increases which is consistent with the obtained results [10].

3.2. Photocatalytic activity

In a typical photocatalytic degradation experiment, CYN at an initial concentration of $1\mu\text{M}$ was degraded under UV-Vis irradiation with as-prepared TiO_2 catalysts (0.25 g L^{-1}). The degradation percentage (DP %) could be estimated as follows [32,33]:

$$\text{DP \%} = \left[\frac{(\text{C}_0 - \text{C})}{\text{C}_0} \right] \times 100\% \quad (2)$$

where C_0 (mg L^{-1}) is the initial CYN concentration, and C (mg L^{-1}) is the CYN concentration after irradiation for certain time. Fig. 8(A, B and C) reveals that the photocatalytic performance for CYN degradation via TiO_2 /UV-Vis photocatalysis depends on phase structure, composition, surface area and optical properties of the as-synthesized TiO_2 samples. Noticeably, the CYN removals with bi-phase anatase-brookite mixtures were significantly higher compared with those of pure anatase and pure brookite. The CYN degradation (%) over bi-phase anatase-brookite mixtures increased when brookite phase content decreased. The h2 sample having the highest surface area and absorption edge, as well as the lowest band gap and PL intensity, exhibited the highest efficiency, achieving complete CYN removal (100%) under UV-Vis irradiation for 15 min, as displayed in Fig. 8(A).

As shown in Fig. 8(B), the photocatalytic degradation curves of CYN followed the first order kinetic model, as given in Eq. (3) [34]:

$$-\ln\left(\frac{\text{C}_t}{\text{C}_0}\right) = k t \quad (3)$$

Where, C_t (mg L^{-1}) is the CYN concentration at time t (min), C_o (mg L^{-1}) is the initial CYN concentration and k (min^{-1}) is the reaction rate constant. The reaction rate constants (k , min^{-1}), could be estimated from Eq. (3) by plotting $\ln(C_t/C_o)$ versus irradiation time, as shown in Fig.8(C), and used to compare the photocatalytic activity of TiO_2 powders. The reaction rate constant of ABH- TiO_2 samples was higher than that of single phase TiO_2 samples, and the sample h2 showed the highest 1st order reaction rate constant (0.18 min^{-1}). Mean values of normalized concentration (C_t/C_o), reaction rate constants (k , min^{-1}), reaction rates (r_o , μMmin^{-1}), R^2 values and CYN degradation percentage (DP %) are summarized in Table 2. The enhanced photocatalytic activity of the h2 sample containing 61.8% anatase/38.2% brookite phases is due to several reasons:

- I) The synergistic effect [10,11,19,35-41] which, can be attributed to the difference in the conduction band edges of the two phases (anatase and brookite phases), which may promote interfacial electron transfer from brookite to anatase, and the resulting energy barrier would suppress back electron transfer, which decreases the probability of the charge carriers recombination [41], confirmed by the low PL intensity.
- II) The high crystallinity and the mesoporosity of the h2 sample can help in the enhancement of its photocatalytic activity as CYN molecules are easily transported and diffused to the active sites of the mesoporous TiO_2 .
- III) The h2 sample has the highest surface area ($62.3 \text{ m}^2\text{g}^{-1}$). The good crystallinity and large surface area may also facilitate the contact probability of catalyst surface and CYN, enhance the active site of the response and accelerate the photocatalytic degradation reaction of CYN aqueous solution. The large surface area leads to high concentration of surface hydroxyl groups which can trap the photo-generated holes and thus decrease the electron hole recombination process [39,42,43]. The electron transfer in the ABH- TiO_2 is displayed in Scheme 1.

4. Conclusions

In conclusion, single phase-titania and anatase-brookite heterojunction TiO_2 were obtained by hydrothermal treatment of $\text{Ti}_2(\text{SO}_4)_3$ aqueous solutions in the absence and presence of glycine, respectively. The brookite/anatase ratios can be well-designed by altering the glycine concentration. The physicochemical characteristics of the obtained TiO_2 samples could be characterized by advanced analysis techniques. The photocatalytic activity of the as-prepared TiO_2 photocatalysts was estimated by CYN degradation in aqueous solution. The results indicated that the photocatalytic activity of ABH- TiO_2 is higher than that of single phase- TiO_2 for the degradation of CYN. The sample (h2) containing 38.2% brookite and 61.8% anatase exhibited the highest efficiency for removal CYN, and its effectiveness was readily explained by a synergistic effect between anatase and brookite TiO_2 phases.

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Figure captions

Fig. 1. (A) XRD patterns of as-synthesized nanocrystalline TiO_2 powders; (B) Relationship between phase contents of TiO_2 samples and the applied concentration of glycine.

Fig. 2. Raman spectra of h1, h2, h3, h4 and h5 samples and inset shows the main peaks.

Fig. 3. FT-IR of h1, h2, h3, h4, and h5 catalysts.

Fig. 4. N_2 adsorption–desorption isotherms of as-synthesized nanocrystalline TiO_2 powders.

Fig. 5. PL of h1, h2, h3, h4, and h5 powder samples.

Fig. 6. (A) The UV–Vis diffuse reflectance spectra; (B) the corresponding Kubelka–Munk transformed reflectance spectra of the products.

Fig. 7. FE-SEM images of different samples obtained: A (h1), B (h5) and C (h2).

Scheme 2. Possible mechanism of TiO_2 phases formation

Fig. 8. (A) Removal efficiencies of CYN under UV light irradiation with TiO_2 ; (B) C/C_0 versus irradiation time; (C) $\ln (C/C_0)$ versus irradiation time.

Table 1. Reaction condition, phase content and characteristics of TiO₂ samples.

Sample	Glycine	Basic	Phase content		^a Crystallite		^b S _{BET}	Pore	Average	Band
ID	concentration	medium	fraction (wt %)		Size (nm)		(m ² g ⁻¹)	volume	Pore size	gap
			A	B	A	B		(cm ³ g ⁻¹)	(nm)	(eV)
h1	0.00 M	NH ₄ OH	100	0	57.8	-	32.3	0.19	5.5, 24.5	3.2
h2	3.2 M	NaOH	61.8	38.2	24.8	76	62.3	0.32	34.5	3.17
h3	1 M	NaOH	43.5	56.5	43	47	39.6	0.12	0.95	3.19
h4	0.5 M	NaOH	38	62	43.9	51	34	0.08	0.5-1.5	3.2
h5	0.00 M	NaOH	0	100	-	59	27.9	0.07	1-1.5	3.26

^a Based on XRD analysis using the Scherrer equation: crystal size = $0.9\lambda/(\beta \times \cos\theta)$, where $\lambda = 0.154$ nm, θ is the Bragg angle, and β is the full wide at half the maximum intensity (FWHM) for the main peaks (101) and (121) for anatase phase and brookite phase, respectively.

^bS_{BET}, Surface area.

Table 2. Raman vibration bands observed and corresponding assignment of h1, h2, h3, h4 and h5 samples at 532 nm excitation wavelength.

Samples	Assignment [Peak position (cm ⁻¹)]	
	Anatase	Brookite
h1	Eg [144.4, 199, 641], B1g [399, 518], A1g [518]	—
h2	Eg [145.5, 199, 639], B1g [513], A1g [513,411]	Ag [199, 639], A1g [249, 411], B1g [215, 325, 497, 513], B2g [585]
h3	Eg [145.3, 199, 639], B1g [518], A1g [518,398]	Ag [199, 639], A1g [248, 398], B1g [215, 325, 458, 518], B2g [358], B3g [287]
h4	Eg [145, 198, 638], B1g [515], A1g [515,410]	Ag [198, 638], A1g [247, 410], B1g [216, 323, 496, 515]
h5	—	Ag [196, 636], A1g [152.5, 249, 399], B1g [216, 323, 466, 498], B2g [366, 465, 587],

		B3g [278, 546]
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Table 3. Average values of C/C_0 as well as 1st order reaction rate constant (k , min^{-1}), 1st order reaction rates (r_0 , $\mu\text{M}/\text{min}$), R^2 and CYN removal efficiency.

Sample ID	C/C_0	k (min^{-1})	$r_0 \times 10^{-3}$ μMmin^{-1}	R^2	CYN removal efficiency (%)
h1	0.816	0.03	31	0.991	47
h2	0.429	0.18	175	0.999	100
h3	0.689	0.05	49	0.950	59.9
h4	0.767	0.04	43	0.985	56.2
h5	0.947	0.01	13	0.964	25.9

Scheme. 1

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6

Fig. 7

Scheme 2

Fig. 8

Scheme. 1