

Research Article

Synthesis of Visible-Light-Activated Yellow Amorphous TiO₂ Photocatalyst

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Visible-light-activated yellow amorphous TiO₂ (yam-TiO₂) was synthesised by a simple and organic-free precipitation method. TiN, an alternative precursor for TiO₂ preparation, was dissolved in hydrogen peroxide under acidic condition (pH~1) adjusted by nitric acid. The yellow precipitate was obtained after adjusting pH of the resultant red brown solution to 2 with NH₄OH. The BET surface area of this sample was 261 m²/g. The visible light photoactivity was evaluated on the basis of the photobleaching of methylene blue (MB) in an aqueous solution by using a 250 W metal halide bulb equipped with UV cutoff filter ($\lambda > 420$ nm) under aerobic conditions. Yam-TiO₂ exhibits an interesting property of being both surface adsorbent and photoactive under visible light. It was assigned to the η^2 -peroxide, an active intermediate form of the addition of H₂O₂ into crystalline TiO₂ photocatalyst. It can be concluded that an active intermediate form of titanium peroxo species in photocatalytic process can be synthesised and used as a visible-light-driven photocatalyst.

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1. INTRODUCTION

Titaniumdioxide(TiO₂)has been the prevailing material in the fields of photocatalysis and solar energy conversion due to being chemically and biologically inert and environmentally friendly. Although TiO₂ is now used in various practical applications, only a small UV fraction of solar light can be utilised because of its large band gap of 3.2 eV. The development of a titania-related photocatalyst that shows a high level of activity under visible light would therefore be a major advance. Yellow TiO₂ prepared by nitrogen doping has been regarded as a visible-light-sensitive photocatalyst [1–4] as well as Cr or V doped TiO₂ [5, 6]. Additionally, metal ion doped SrTiO₃ [7–9], some metal sulfides such as AgGaS₂ and AgInZn₇S₉ [10], (Ga_{1-y}Zn_y)(N_{1-x}O_x) [11], and Sm₂Ti₂O₇ [12] have been reported as visible-light-driven photocatalysts. There may be some disadvantages of doped materials, for instance, low surface area because of using high temperature, the requirement of the expensive chemicals and synthetic methods, and an increase in carrier recombination.

Amorphous TiO₂ is of interest for photocatalysis because of its high surface area and high adsorption. Moreover,

simple synthesis with elimination of the calcination step would mean lower costs for chemicals and energy consumption. There have been only a few works that studied or mentioned amorphous TiO₂. Among them, it was found that commercial amorphous TiO₂ had negligible photoactivity because it contains high concentrations of defects which cause rapid e⁻-h⁺ recombination [13]. However, synthetic amorphous TiO₂ has been recently shown to exhibit significantly photoactivity rates in aqueous methanol solutions under full solar spectrum (200 to >1000 nm) using a 400 W Xe arc lamp [14].

Hydrogen peroxide (H₂O₂) has been reported as an important factor in the photocatalytic process because it has occurred as an intermediate in the mechanism of the photocatalytic process using TiO₂ as photocatalysts, and it has been reported that the reactivity can be accelerated by the addition of H₂O₂ [15–17]. Moreover, titanium-peroxo species were found to be the active species in the titanium silicalite-1 (TS-1)/H₂O₂/H₂O system for partial hydrocarbon oxidation [18, 19]. In general, titanium-peroxo species or aqueous peroxotitanate are yellow or yellow-green depending on pH. There have been some works that used

titanium peroxo complex as a starting material for TiO_2 preparation [20–22].

As mentioned in the above discussion, H_2O_2 is important in photocatalysis at TiO_2 , amorphous TiO_2 offers some enhancement of activity and noting the yellow colour of the catalytically active titanium-peroxo species in the $\text{TS-1}/\text{H}_2\text{O}_2/\text{H}_2\text{O}$ system, it would be interesting to see if yellow amorphous titanium-peroxo species can act as a photocatalyst under visible light. In this work, therefore, we investigate the visible-light-driven photoactivity of yellow amorphous TiO_2 (hereinafter referred to as “yam- TiO_2 ”) prepared by a peroxide-based route, using titanium nitride (TiN) as a precursor.

2. EXPERIMENTAL

2.1. Materials

Yam- TiO_2 was synthesised by a peroxide-based route using TiN as precursor. 50 mL of 30% H_2O_2 (Fisher Scientific, Leicestershire, UK) was added to 1.0 g of TiN (Alfa Aesar, Lancashire, UK) under acidic condition ($\text{pH} \leq 1$) adjusted by HNO_3 acid solution. After aging at room temperature without any stirring for 24 hours, a clear red-brown solution was obtained. The obtained precursor solution was stable for several days under ambient atmosphere. Yellow precipitate is formed from this solution after adjusting the pH of the solution to 2 by slowly adding ammonia solution with the constant stirring. The precipitate was filtered and washed with distilled water several times. It was then dried at room temperature. The dried powder was also calcined at a constant heating rate of $5^\circ\text{C}/\text{min}$ at various temperatures and held at these temperatures for 2 hours.

XRD data were collected with a Stoe Stadi-P Transmission X-ray diffractometer, using $\text{Cu K}\alpha_1$ radiation in the range $2\theta = 20\text{--}80^\circ$. The BET surface area measurement and pore analysis were carried out by nitrogen adsorption with use of Micromeritics ASAP 2020 V3.00 H surface area analyser. The measurement was carried out at liquid nitrogen temperature after degassing the powder sample at 120°C . TEM imaging was obtained using a JEOL-JEM 2011 electron microscope. Diffuse reflectance spectroscopy was carried out with a Perkin Elmer Lambda35 UV/Vis spectrometer using BaSO_4 as a reference.

2.2. Evaluation of photocatalytic activity

Visible light activity was evaluated on the basis of the decomposition of methylene blue (MB) in an aqueous solution. The sample powder was suspended in 200 mL of an 1×10^{-4} M MB solution by air bubbling. This mixture was first suspended in the dark for 2 hours to reach the adsorption equilibrium before irradiation with a high intensity discharge 250 W iron doped metal halide UV bulb (UV Light Technology Ltd., Birmingham, UK) equipped with UV cutoff filter, $\lambda \geq 420$ nm (Borosilicate Coated Glass HM07, UQG(optic)Ltd., Cambridge UK). The mixture temperature was controlled at about 25°C using a water bath for infrared radiation and lamp heating removal. After irra-

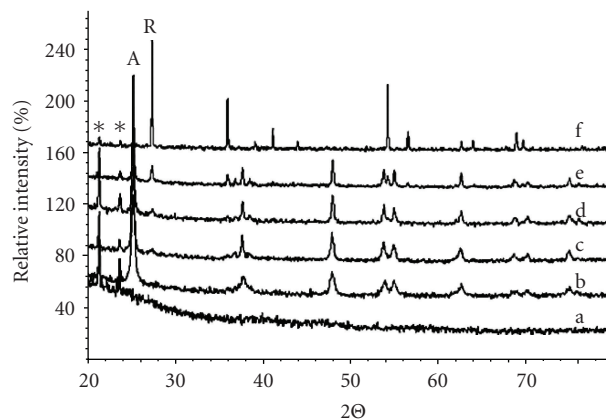


FIGURE 1: XRD patterns of as-prepared yam- TiO_2 (a) and after calcined at temperatures of (b) 400°C , (c) 800°C , (d) 850°C , (e) 900°C , (f) 1100°C (*: Vaseline specific peaks, A: anatase, R: rutile).

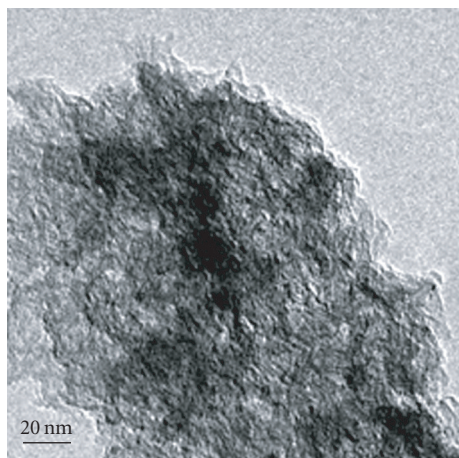
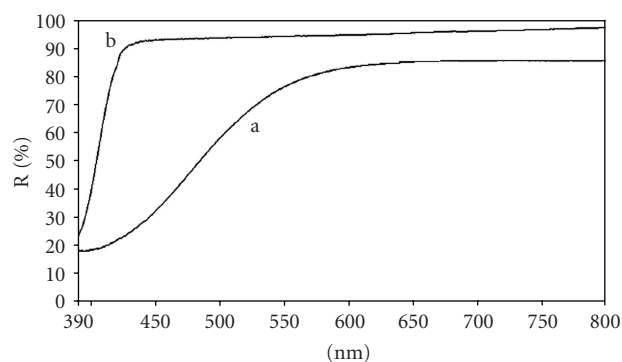
diation, 2 mL of the mixture was collected and centrifuged at the irradiation time intervals (hourly). The photoactivity was examined by monitoring the reduction of the absorbance at 665 nm. The spectrophotometric measurements were carried out using Perkin Elmer Lambda35 UV/Vis spectrometer. A ten-fold dilution was used for the high absorbance solutions.

3. RESULTS AND DISCUSSION

3.1. Characterisation

The XRD pattern of the as-prepared powder confirmed the amorphous structure of yam- TiO_2 as no diffraction peaks can be observed, Figure 1. Yam- TiO_2 was quite stable under air atmosphere (the sample used throughout this work was kept for several months in the aerobic vial). However, colour and phase transformation of yellow amorphous to white anatase/rutile occurred on heat treatment. Anatase was presented after calcination at 400°C and remained as a major phase until 900°C . This indicated that a high temperature stable anatase phase can be produced by this method. Phase transformation from anatase to rutile can be observed at about $800\text{--}850^\circ\text{C}$ which was higher than TiO_2 prepared by conventional methods.

Furthermore, it was found that the particle sizes of TiO_2 after calcination at 600 and 900°C calculated by Scherrer equation were 31 and 51 nm, respectively. The obtained phase transformation temperature and particle size were consistent with the previous work that synthesised TiO_2 by peroxide-based route and using H_2TiO_3 as precursor [20]. However, the stability of anatase phase in this work was higher than TiO_2 synthesised by the peroxide-based route using TiCl_3 as precursor [21]. The peroxide-based route, therefore, is interesting for TiO_2 preparation because of the high temperature anatase-rutile phase transformation; however, it depends on precursor and synthesis condition. TiN is interesting to be used as an alternative precursor in a peroxide-based route because of its air and moisture stability, organic and chloride ion-free route, simplicity, and low cost.

FIGURE 2: TEM image of as-prepared yam-TiO₂.FIGURE 3: The UV-Vis diffuse reflectance of (a) yam-TiO₂, (b) commercial rutile TiO₂.

According to our focus on evaluation of the visible light photoactivity of yellow amorphous TiO₂, TEM, BET and diffuse reflectance were only examined with the as-prepared powder. Figure 2 shows the TEM image of the as-prepared powder. The ultrafine particles with amorphous structure can be seen. As a result, a high BET surface area of 261 m²/g was obtained. The diffuse reflectance spectrum shows the red shift of the absorption edge into the visible region (Figure 3(a)) compared with commercial rutile TiO₂ (TIOXIDE) (Figure 3(b)).

Yam-TiO₂ is attributed to the η^2 -peroxide (η^2 -TiOOH) because of the similar red shift and that yam-TiO₂ transformed to white powder on heating similar to the η^2 -titanium peroxospecies in the TS-1/H₂O₂/H₂O system reported by Bonino et al. [18]. Lin and Frei [19] found that the η^2 -peroxide species obtained upon loading H₂O₂ into TS-1 was photodissociated efficiently under irradiation with visible or near UV light. Moreover, η^2 -peroxide was assigned to the adsorption structure formed by the addition of H₂O₂ on the surface of rutile TiO₂. This structure was preferable to produce hydroxyl radical that accelerates the photoactivity [17].

3.2. Visible light photocatalytic activity

The photobleaching of MB has been widely studied in heterogeneous photocatalysis. However, there are some con-

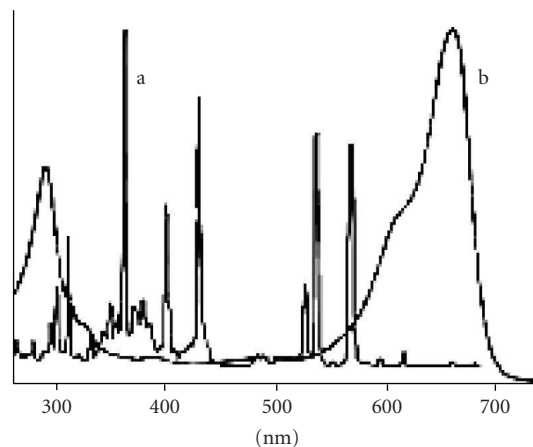
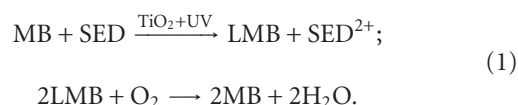


FIGURE 4: The emitting wavelength of metal halide lamp (a) and UV-Vis absorption spectrum of MB (b).

cerns about the bleaching of MB due to the photoreduction to colourless form and photoabsorption of MB [23–25]. There are two main forms of MB, the blue colour of oxidised form (MB) and the colourless reduced form (leuco form, LMB). MB can be photoreduced to LMB by TiO₂ under UV light under anaerobic condition and in the presence of a sacrificial electron acceptor (SED). It was found that MB itself can act as an SED. However, this process is reversed on the addition of O₂ to the anaerobic system. Although LMB is readily oxidised back to MB by oxygen, this reaction depends on pH. The rate increases with pH, LMB is moderately stable under acidic condition but reacts rapidly with air under basic condition [23]:



As continuous air bubbling of a neutral solution was utilised in this work and no reducing agent was added to the system, it is likely that the dominant bleaching process is the photomineralisation of MB rather than the reductive formation of LMB. This system, MB/TiO₂/air-saturated water system, has widely been utilised for the demonstration of semiconductor photocatalysis, as reviewed by Mills and Wang [23]. It is possible or even probable that partial rather than complete mineralisation into CO₂, NH₄⁺, NO₃⁻, and SO₄²⁻ is occurring as the main observable in bleaching MB.

The photoabsorption of MB can be an issue for visible-light-driven photocatalyst investigation because MB can absorb visible light, especially, in the range 600–700 nm. Yan et al. [25] concluded that MB was not an appropriate substrate for a visible-light photocatalytic activity test particularly in the range of 540–680 nm irradiation. However, the most important and intense emitting wavelength of the metal halide lamp used in this work is in the range of about 200–580 nm [26]. After equipping with a UV cutoff filter, the emitting wavelength is in the range of 420–580, which has little overlap with the absorption of MB as shown in Figure 4.

As a result, the photoabsorption of MB should not significantly effect the determination of visible light photocatalytic activity test in this work.

Figure 5 shows the photocatalytic degradation of MB comparing between amorphous TiO_2 prepared in acidic condition (yam- TiO_2) and in basic condition (labeled byam- TiO_2), including blanktest (2×10^{-5} M MB). It was found that 10% bleaching of MB was shown after visible light irradiation of only MB for 5 hours (Figure 5(a)), whereas slightly higher, 15% photobleaching of MB, was obtained by using 0.5 g/L byam- TiO_2 as photocatalyst (Figure 5(b)). However, the latter amount was obtained after 45% of 1×10^{-4} M MB was adsorbed, that indicated that the initial concentration of MB before photobleaching was about 5.5×10^{-5} M. Comparison with using 0.5 g/L yam- TiO_2 , about 97% adsorption and 2% photocatalytic activity was measured (Figure 5(c)). It can be concluded that the adsorption capacity of yam- TiO_2 was significantly higher than byam- TiO_2 ; however, the extent of adsorption must hinder the heterogeneous photoactivity. Therefore, a decreased amount of yam- TiO_2 to 0.2 g/L was performed for photoactivity comparison (Figure 5(d)). It can be seen that about 46% photobleaching of MB after adsorption was obtained, which was considerably higher than using byam- TiO_2 in spite of using less amount and higher concentration remained after adsorption. Moreover, only 9% photobleaching was observed for 0.5 g/L of Degussa P25 in 1×10^{-5} MB under visible light for 2 hours (compared to 93% under UV for 1 hour) showing that the yam- TiO_2 was much more effective, $\sim 40\%$ under visible light for 2 hours. An important point to note is that the adsorbed MB seemed much less intense in colour and indeed the colour had changed to pale purple/violet. This could indicate an oxidative adsorption process in the dark with the oxidised form, MB^{++} being formed and adsorbed onto the yam- TiO_2 ; however, confirmation requires further study.

The irreversibility of the photobleaching process on continuous air bubbling for 24 hours in the dark after complete decolourisation of MB and the disappearance of the bands associated with MB (294 nm and 665 nm) with no appearance of band associated with LMB (256 nm) [24] as shown in Figure 6. were observed, further confirming that photoreduction of MB to LMB was not the dominant process.

These results show that yam- TiO_2 can act as a visible-light-driven photocatalyst better than byam- TiO_2 , in parallel with a red shift of the absorption edge into the visible region as shown in Figure 7. However, an increase in visible absorption edge does not guarantee consistency in visible light photoactivity, the recombination and surface area are also important factors.

Recyclability and stability of photocatalyst are important factors for any practical applications. Therefore, we have attempted to investigate cyclability and stability. In general, the photoactivity of crystalline TiO_2 is observed by monitoring the degradation of MB in an aqueous solution, and adsorbed MB is not an issue probably due to small amount of MB that was adsorbed on crystalline TiO_2 . The recyclability of crystalline TiO_2 normally performed by elimination of adsorbed MB on TiO_2 by oxidation

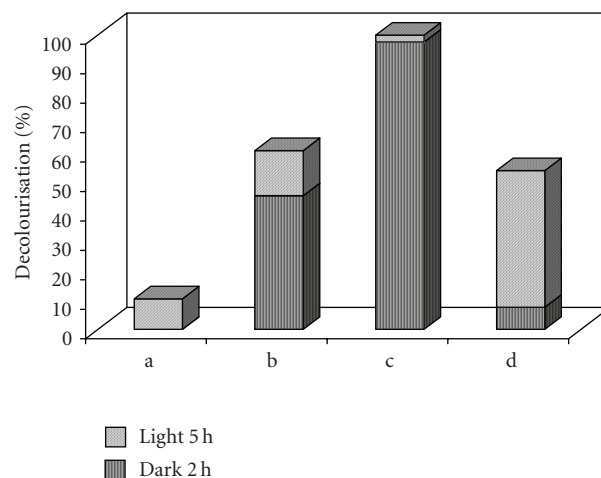


FIGURE 5: % decolourisation of MB under the condition of dark 2 hours and light 5 hours of (a) MB, (b) MB + 0.5 g/L byam- TiO_2 , (c) MB + 0.5 g/L yam- TiO_2 , (d) MB + 0.2 g/L yam- TiO_2 .

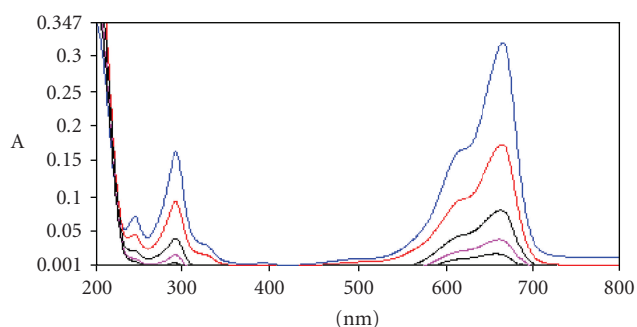


FIGURE 6: UV-Vis absorption spectra of MB.

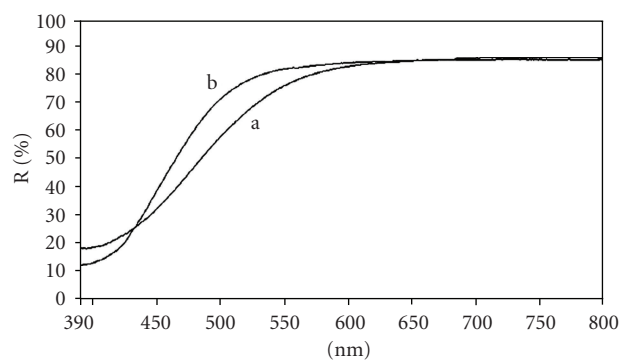


FIGURE 7: The UV-Vis diffuse reflectance of (a) yam- TiO_2 , (b) byam- TiO_2 .

at temperatures higher than about 200°C , which is the decomposition temperature of MB. However, removal of adsorbed MB by calcination cannot be used in the case of amorphous form because crystallisation will be induced.

As a result, the cyclability of yam- TiO_2 was measured by two different methods, with and without removal of

adsorbed MB. The first way, to completely remove adsorbed MB on the surface by using photoactivity itself until the original colour of yam-TiO_2 was recovered. Due to a large amount of MB being adsorbed on the surface, 48 hours UV irradiation was used for adsorbed MB removal, after colourless solution was obtained by visible light photoactivity test, in order to reduce the duration of adsorbed MB removal and to evaluate the stability of yam-TiO_2 under UV light simultaneously. Figure 8 shows the recyclability by using UV irradiation for adsorbed MB removal. The 0.5 g/L ratio of catalyst to volume of MB was chosen because of the incomplete MB adsorption, hence, the visible-light photoactivity can be monitored, and a quantity of catalyst will be sufficient for removal of the high amount of adsorbed MB in 48 hours. About 97% adsorption and 2% photoactivity in 5 hours were obtained in the preliminary photoactivity test (Figure 8(a)). After the mixture was irradiated with UV light for 48 hours, the violet powder of visible light irradiated/adsorbed MB was changed to yellow powder as the original colour with a small amount of violet specks. Some violet specks indicated incomplete removal of adsorbed MB. Thereafter, the colourless aqueous solution was removed from the mixture by rinsing and the remaining powder left to dry at room temperature.

The first reuse was performed by readding 200 mL of 1×10^{-4} M MB. A slight decrease of adsorption and photoactivity was obtained for the first and second recycles (Figure 8(b), (c)). A small decrease of adsorption capacity and photoactivity presumably caused by incomplete adsorbed MB removal and decrease of efficiency or stability of amorphous structure after prolonged UV irradiation, which the colour changing from yellow to pale yellow can be observed by the naked eye (XRD data showed that it remained amorphous structure). However, if considering only photoactivity by using MB concentration after adsorption, about 2×10^{-5} M estimated from the percentage of bleaching, as an initial concentration, about 80% bleaching of MB under visible light irradiation can be reached in 5 hours both in the first and second recycles (Figure 8(d), (e)).

The second way of recyclability testing was performed by readding 200 mL 1×10^{-4} M MB without removal of adsorbed MB. The results are shown in Figure 9. The adsorption capacity significantly decreased in the first and second reuses as expected, 75% and 22%, respectively (Figure 9(b), (c)), due to MB was adsorbed 97% of 1×10^{-4} M MB in the preliminary photoactivity test before recycling (Figure 9(a)). The photobleaching of MB in the first reuse, including adsorption and photoactivity, was 85% in 4 hours and 99% in 24 hours (Figure 9(b)), while 51% and 95%, respectively, in the second reuse (Figure 9(c)). However, considering only the photoactivity, the percentage of bleaching of MB under visible light irradiation can be about 40% in 5 hours and more than 90% in 24 hours both in the first and second recycles (Figure 9(d), (e)). These results show the reusability of yam-TiO_2 .

As mentioned above about the gradual colour changing of yam-TiO_2 from yellow to pale yellow after irradiation, it was found that it remained pale yellow and can be a visible-

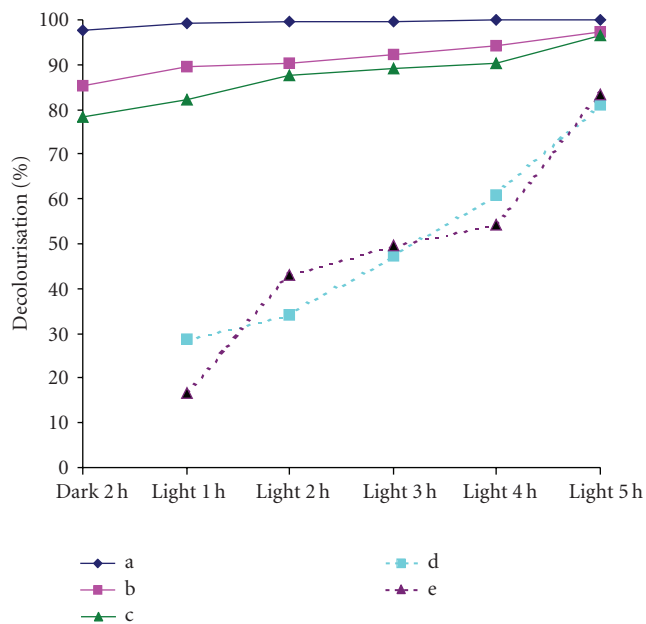


FIGURE 8: Recyclability with removal of adsorbed MB (a) MB + 0.5 g/L yam-TiO_2 , (b) 1st reuse, (c) 2nd reuse, (d) only photoactivity of 1st reuse, (e) only photoactivity of 2nd reuse.

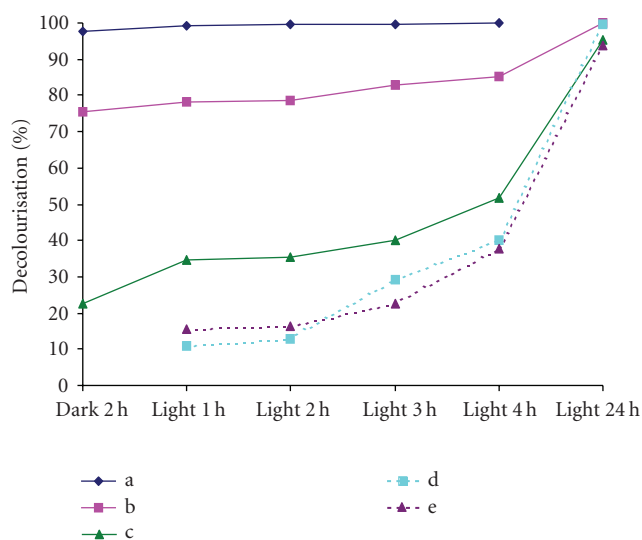


FIGURE 9: Recyclability without removal of adsorbed MB (a) MB + 0.5 g/L yam-TiO_2 , (b) 1st reuse, (c) 2nd reuse, (d) only photoactivity of 1st reuse, (e) only photoactivity of 2nd reuse.

light-driven photocatalyst even on prolonged irradiation, although the reaction rate decreased. The color change probably due to some η^2 -peroxide being converted to a hydroxide form upon photo irradiation [17, 19]. The intense yellow can be recovered after further addition of H_2O_2 as well known for crystalline TiO_2 . For this reason, yam-TiO_2 can be reused several times with addition of H_2O_2 .

4. CONCLUSION

An active intermediate form of an addition of H_2O_2 into crystallized TiO_2 photocatalyst can be synthesised by peroxide-based route. It can be used as a visible-light-driven photocatalyst itself with the high surface area of amorphous form.

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