Research article
International Journal of Heterocyclic Chemistry,
Vol. 9, No. 2, pp. 80-100 (Spring 2019)
© Islamic Azad University, Ahvaz Branch
http://ijhc.iauahvaz.ac.ir

Study of structural and optical properties of anthocyanin-modified TiO_2 for the purpose of photodegradation

Marzieh Ataie Dil[a,b], Azadeh Haghighatzadeh[b*]

[a] *Department of Physics, Khozestan Science and Research Branch, Islamic Azad University, Ahvaz, Iran*

[b] *Department of Physics, Ahvaz Branch, Islamic Azad University, Ahvaz, Iran*

Abstract

In this research, dye – sensitization method was used to improve the photocatalytic activity of titanium dioxide dye using natural pigment of anthocyanin. Product morphology were studied by scanning electron microscopy (SEM) and phase identification using X-ray diffraction (XRD) analysis. Spectroscopic analysis of the matter was performed using FT-IR spectrometer and UV-Vis spectrophotometer. Analysis of DRS was used to study the optical properties of the samples. The results of XRD and SEM showed that the surface modification of titanium dioxide with pigments has no effect on the crystalline phase and morphology of particle. Analysis of DRS showed that dye – sensitization caused reduction in energy gap and can shift the absorption edge of TiO_2 to the visible region. The photocatalytic activity of the modified TiO_2 was studied by measuring the degradation percent of methylene blue under visible light irradiation and the effect of various parameters on the amount of degradation of methylene blue too.

Keywords*:* Photoreaction, Catalysts/Catalysis, Titanium dioxide, Dye- modified.

Introduction

Nowadays, the municipal and industrial wastewater treatment systems is not being used suitably which is a serious threat to surface and underground water resources. Notable point about the industrial wastewater is that, their outputs are hard degradable and conventional methods of treatment are not able to reduce their pollution. Therefore, use of new technologies with high efficiency and low cost can provide a good base for meeting this target. One of the newest and best technology that using nanoscale particles has high efficiency on removing contaminants, is the use of catalytic processes of nanoparticles that is done under light radiation with the use of a semiconductor. In recent years, Titanium dioxide (TiO_2) as a photocatalyst for degrading organic pollutions has attracted much attention which is due to its various advantages. Unfortunately, technological use of TiO_2 is limited by its wide band gap, which requires UV light radiation (3% of the solar spectrum) to obtain its photocatalytic activity [1]. In order to overcome this limitation, continuous efforts have been taken to promote the photocatalytic activity and enhance the visible light response (46% of solar spectrum). These techniques include doping with cation /anion, sensitization with dye, coupling with another small band gap semiconductor and implantation of metal ion [2]. Surface modification method by natural dyes, which was used in this study, is cost-effective and environmentally friendly than other methods, which has recently been of interest to researchers and in particular, conservationists [3]. Recently (in 2016), Pouretedal et al. was able to remove high percentage of Paranitrophenol from aqueous solutions with the use TiO_2/ZnS nanocomposite sensitized with bromothymol blue [4]. Janytabr et al in a report published in 2014, studied the mechanism of TiO_2 and ZnO photocatalysts sensitized with Merbromin on removing phenol [5]. In another study conducted in 2012 by Chaudry et al, degradation of phenol was performed using y eosin dye-sensitized TiO_2/Pt photocatalysts and it was removed from the aquatic environment [6]. The main purpose of this paperis to improve the photocatalytic properties of Titanium dioxide using natural anthocyanins pigments to visible light response and optimizing the parameters involved in the experiment.

Experimental section

Materials and apparatuses

Materials used in this study consisted of anatase phase titanium dioxide nanoparticles which was supplied by Us-Nano Company, ethanol 99.5% purchased from Samchon Company South Korea and anthocyanin pigment derived from hibiscus tea plant that was used for preparation of photocatalyst sensitized to the pigment for activity in the visible region of the electromagnetic spectrum. Photocatalytic activity test was performed by photo-reactor made of a metal halide lamp [150 *w*], A UV cut-off filter to remove UV radiation, a magnetic stirrer and an electric fan for cooling and air conditioning. The spectrophotometer DR5000 was used to evaluate the absorption spectra of samples and study their photocatalytic activity.

Method

Preparation of dye-modified TiO_2

In the first phase with the aim of providing pigment, 6 *g* of hibiscus tea powder was added to 50 *ml* of 99.5% ethanol and the mixture was placed inside the refrigerator for 48 hours; Finally, anthocyanin pigment of hibiscus tea was extracted by filtering the ethanolic solution from a filter paper. In the second step, 2 *g* of titanium dioxide powder was heated at 100°*C* for 4 hours to eliminate water adsorbed on its surface. In the third step, in order to absorb the dye by photocatalyst, nanopowder was added to 50 *ml* of ethanolic solution of anthocyanin and the obtained mixture was kept at ambient temperature for 12hours in the dark. In The next step to remove the unabsorbed pigments from photocatalytic surface, the resulting solution was washed by distilled water and ethanol in the centrifuge and then filtered. At the end, the resulted powder was dried in the oven at 70 ° *C* for 3 hours to fix the pigment on the nano photocatalyst. Crystal structure and phase identification of dye-modified titanium dioxide was studied using the X-ray diffraction (XRD) pattern existent in Tehran University and their morphology through the images obtained by scanning electron microscopy (SEM) tescan – Mira III model existent in Sharif University. In addition, infrared spectroscopy was carried out to determine the links-formed on the surface of the nanoparticles by means of infrared spectroscopy Perkinelmer BX-II model made in America available in the Islamic Azad University of Ahvaz. In order to study optical properties and to calculate the energy gap, the reflectance spectra was evaluated by UV-vis spectrophotometer Model Avaspec-2048-TEC avalamp DH-S Setup available in Sharif University laboratory center.

Photocatalytic activity

At all steps of photocatalytic process, experiments were performed in 250 *ml* of methylene blue solutions with concentration, PH and specified amount of catalyst to determine the optimal parameters for the removal of methylene blue. In each step of optimization, solution was stirred for 20 *min* under the dark condition for adsorption - desorption equilibrium and finally exposed to radiation visible- light in the photoreactor. To measure the reduction of concentration of methylene blue in the photocatalytic system at intervals of 30 minutes, 5 *ml* of the solution was removed and was centrifuged at 3000 *rpm* for 10 minutes to separate the catalyst particles and the concentration of methylene blue was determined using the spectrophotometer at the wavelength of maximum absorbance (λ_{max}=663*nm*). The percentage degradation was determined from the Eq. (1).

$$D = \frac{(A_0 - A_t)}{A_0} = \frac{(C_0 - C_t)}{C_0} \cdot 100 \qquad (1)$$

Where C_0 and C_t are the initial concentration and concentration at time t, A_0 and A_t are initial and final absorbance at time t, D is the degradation efficiency[7] .

Calculation of degradation rate constant of the reaction is another way to check the photocatalytic activity of nanoparticles. According to the kinetic studies conducted on the photocatalytic decomposition of methylene blue, the best assumption is that the mechanism of dye degradation has been considered as a pseudo first order reactions. In this case, the reaction kinetics is calculate based on equation (2).

$$-\ln\left(\frac{C_t}{C_0}\right) = kt \qquad (2)$$

In the above equation, k is the reaction rate constant of first-order model, t is irradiation time, C_0 and C_t are the initial concentration and concentration at time t [8].

Results and discussion

Structural and optical properties

In this section to review and analysis modification method proposed, structural and optical analysis were carried out and the results were presented. In order to ensure the proper selection of pigments, in the first stage of experimental analysis, spectrophotometer UV-vis was performed Fig.1. Shows the intensity changes of anthocyanin pigment absorption as a function of the absorbed wavelength in the wavelength range of 200 to 800 *nm*. Considering Fig.1, the highest absorption of anthocyanin pigment in the ultraviolet is at the wavelength 330 *nm* and the highest absorption of anthocyanin pigment in the visible region is at the wavelength 550 *nm*. Appendix of Fig.1 displays the dye bands of visible region wavelength of the electromagnetic spectrum. The results of Fig.1 clearly shows the appropriateness of anthocyanin pigment for modification of titanium dioxide photocatalysts to increase the performance in the visible region due to the high absorption ability of visible light.

In the second step of empirical analysis, structural properties of titanium dioxide nanoparticles was studied by X-ray diffraction pattern. X-ray diffraction pattern for non-modified and modified particles with dye have been shown in Fig.2. The results of X-ray diffraction patterns of the samples were investigated using Xpert software and XRD standard card No. 00-021-1272 for anatase phase. According to Fig.2, the existence of plates (101), (103), (004), (112), (200), (105), (211), (204), (220), (116) and (215) at the angles 2θ= (25.38), (36.98), (37.81) ,(38.46), (48.15),(53.97), (55.22), (62.79), (68.87), (70.36), (75.16) state that purchased and modified samples have anatase structure. Therefore, according to Fig.2 it can be concluded that modification of the surface of photocatalysts using anthocyanin pigment had not changed the crystalline phase structure. X-ray diffraction pattern with Debyee-Scherrer equation according to equation (3) for each main peak provided the possibility to calculate the crystallite size of prepared samples.

$$D = \frac{(0.9\lambda)}{\beta \cdot \cos\theta} \qquad (3)$$

In equation (3), λ is the wavelength of X-ray diffraction (0.15418 *nm*), β is the full width at half maximum of the diffraction peakand θ is the diffraction angle at the maximum intensity. Equation (3) has shown the average crystallite size for the maximum peak (101) for non modified and dye-modified titanium dioxide as 18.98 and 19.20*nm*, respectively that indicates the dye modification of semiconductor had no effect on the crystalline phase.

In the third step of experimental analysis, to study the effect of dye sensitization on the morphology of nanoparticles surface, the images are obtained from scanning electron microscope. SEM images of non-sensitized and dye-sensitized titanium dioxide nanoparticles with the zoom of 200 *nm* which are shown in Figures 3 a and b, respectively. The results of Fig.3 shows spherical morphology for both non-sensitized and dye sensitized samples, it also shows no change in the morphology behavior of the surface in the presence of dye sensitization process of the photocatalysts.

In the fourth step, structural studies of Fourier transform infrared (FT-IR) spectroscopy is used to study the formed link of pigment on the surface of titanium dioxide. Figures 4 (a) and (b) show the results of infrared spectroscopy of non-sensitized and dye-sensitized nano-powder. Fig.4 (a) for Pure titanium dioxide shows a peak in the region of 750-1400 cm^{-1} related to Ti-O-Ti and absorption peak at 1386 cm^{-1} related to the group (C-OH) [9]. Fig.4 (a) shows the absorption peak in the area of 1610 and 3256 cm^{-1} related to OH stretching vibration due to physical adsorption of water on the surface [10]. According to Fig.4 (b), peaks generated in the curve of infrared spectroscopy of titanium dioxide sensitized with anthocyanin indicates the presence of C = C at 1637 cm^{-1}, C = O at 1780 cm^{-1} and groups of OH at 3419 cm^{-1} related to the benzene ring in the structure of anthocyanin [11] that approve absorption of anthocyanin pigment on the surface of titanium dioxide.

The main purpose of this research is to improve the photocatalytic efficiency of titanium dioxide nanoparticles in the visible region of the electromagnetic spectrum. Therefore, in the final stage of structural and optical studies it is necessary to ensure the shift of energy gap from the ultraviolet to the visible area through the study of energy gap of modified nanoparticles. Fig.5 shows diffusion reflectance spectra (DRS) of non -modified and modified titanium dioxide nanoparticles versus the wavelength in the range of 300 to 800 *nm* wavelength recorded by UV-Vis reflectance spectroscopy device. As expected, the reflection of photons in the visible light region between 400 to 700 *nm* is reduced with dye sensitization which represents an increase in visible photons absorbed by the sensitized photocatalysts. Fig.5 shows that the transmission of spectrum to lower energies and higher wavelengths which is known as red shift happened from the ultraviolet to the visible region for dye-modified Titanium dioxide nanoparticles which is due to the interaction of dye with nanoparticles [4]. Furthermore, the results of Fig.5 for titanium dioxide modified by anthocyanin in the maximum absorption range between 500 to 600 *nm* are in a good agreement with the results of Fig.1 in the visible region for the photon absorption by anthocyanin.

In order to calculate the band gap of titanium dioxide photocatalysts have been used the results of UV-vis reflectance spectra and the equation Kubelka–Munk to convert the reflectance into the equivalent absorption coefficient [12].

$$F(R) = \frac{(1-R)^2}{2R} \qquad (4)$$

The definition of Kubelka–Munk function (F(R)) is as follows: Where R is the reflection coefficient measured from the sample. The energy gap chart can be calculated by replacing equation (4) in the absorption coefficient a of tuk equation (5) and finally the extrapolated linear of the plot versus hv[13] .

$$[ah\nu] = \beta.\left(h\nu - E_g\right)^n \qquad (5)$$

Its results shown in Fig.6. According to Fig.6, the band gap of non-modified and modified nanoparticles using tangent where the horizontal axis is $[F(R).hv]^{1/2}=0$, had been obtained 3.2 and 3 *eV*, respectively. In addition to the energy gap,the absorption wavelength threshold for non-modified and modified titanium dioxide has been obtained from the relation $Eg=hc/\lambda$ is 387 and 418 *nm*, respectively.That represents the displacement of the absorption edge from the ultraviolet region to the visible region. This reduction in the energy gap and an increase in the maximum absorption wavelength in the modified photocatalysts could be attributed to the effect of the surface modification.

Photocatalytic properties

In this part of study the photocatalytic properties of dye-modified Titanium dioxide nanoparticles were evaluated and the different parameters affecting photocatalytic properties, such as time, concentration of contaminants, the amount of photo catalyst and PH, the optimal amount of each of them was studied. In order to evaluate the effect of the time on the removal of methylene blue using the sensitized titanium dioxide by anthocyanin, 250 *ml* of methylene blue solution with a concentration of 10 *ppm*, PH=7 and 0.1*g* catalyst was prepared and put under visible light radiation for 270 minutes. Fig.7 shows the percentage of methylene blue destruction versus time Fig.7. Indicates that the removal of methylene blue from solution has been increased up to 210 minutes, but after 210 *min*, increasing the duration of lighting has no significant effect on the increase of the percentage of degradation of methylene blue by catalysts under visible light. Therefore, duration of 210 minutes is considered as the optimal time of lighting.

Fig.8 shows the percentage of degradation of methylene blue as a function of the dye-sensitized catalyst concentration for 210 minutes radiation of light. In this test, the photocatalytic degradation of the solution has been studied by changing the amount of catalyst from 0.05 to 0.3*g* keeping the methylene blue concentration constant (10 *ppm*) and PH=7. As shown in fig.8, by increasing the amount of catalyst from 0.05 to 0.1 *g*, the process of degradation has been ascending and after that it has almost become constant. Reducing the amount of absorption by increasing the amount of catalyst can be attributed to turbidity of the solution and lack of access to visible light photons. Because at high concentrations of the catalyst (higher than 0.1 *g*), the solution becomes turbid and the light ray is not able to penetrate and interact with photocatalyst. Thus, less number of photocatalysts were activated, leads to aggregation and scattering of light, which leads to decrease in degradation efficiency of MB [14].

Next, the effect of different concentrations of dye have been studied with maintaining constant concentration of photocatalytic (0.1*g*) and PH=7 at 250 *ml* of methylene blue solution with a concentration of 5 to 15 *ppm* for 210 minutes radiation the light. Fig.9 shows the percentage of methylene blue degradation for titanium dioxide sensitized with anthocyanin at different concentrations of methylene blue solution. As observed in Fig.9 with increase in the initial concentration of methylene blue from 5 to 15 *ppm*, the percentage of destruction of methylene blue by titanium dioxide sensitized with anthocyanin reduced. This reduction in removal is because of disability in transition of visible light photons to the photocatalytic surface in the presence of long chains of created complex structure of methylene blue. At high dye concentration some amount of light is absorbed by the dye molecule itself. This results in restricted production of OH^- and $O^._2$ radical which decreases the possibility of degradation of pollution molecule [14,15].

PH of the solution is one of the important parameters for study of Methylene blue degradation. The effect of PH was studied in PH range of 4–12, with keeping the catalyst concentration constant (10 *ppm*) and initial concentration of methylene blue in the range of 0 to 210 minutes of exposure to lightening. To adjust the PH, 0.1 *M* H_2SO_4 solution (acidic range) and 0.1*M* NaOH solution (alkaline range) have been used. Percentage of degradation of methylene blue in different PH for the titanium dioxide catalyst sensitized with anthocyanin is shown in Fig.10. The results of Fig.10 show that at low PH, the removal of methylene blue is less and by increasing the PH (from 4 to 11), the removal rate increased. This increase in degradation was remarkable up to PH=11 (PH=12), but At higher PH, the formation of OH^- radically increased and electrostatic interaction took place between MB (cationic dye) and nanoparticles. It is also one of the result for the decrease in destruction efficiency of methylene blue at PH greater than 11 is repulsion of OH^- ion by the negatively charged photocatalyst surface[14].

study of kinetics of photocatalytic reaction

In the final step of photocatalytic study, degradation reaction rate constant has been studied as a measure of mechanism of the photocatalytic activity of titanium dioxide sensitized with anthocyanin. Fig.11 Shows exponential function curve ($-Ln(C_t/C_0)$) versus time in the presence of dye-sensitized photocatalyst for the initial concentration of methylene blue of 10 ppm and catalyst amount 0.1*g*. In accordance with the results of Fig.11, the exponential function with constant slope reduced by increasing the exposure time and rate constant of degradation is equivalent to ($0.0015\ min^{-1}$) and $R^2=0.9885$, which confirms the pseudo first - order reaction.

Conclusion

In this study, the effects of dye sensitization with anthocyanin on the photocatalytic properties of titanium dioxide were studied to remove methylene blue. The overall objectives of this study was the displacement of photocatalytic performance area of the titanium dioxide from the ultraviolet to the visible region of the electromagnetic spectrum. In this regard, the study of reflectance spectra and calculating of the energy gap of sensitized titanium dioxide showed that sensitization with anthocyanins pigment caused has changed activity area of the titanium dioxide absorption wavelength and has displaced the energy gap of titanium dioxide from 3.2 *ev* to 3 *ev* for titanium dioxide sensitized with anthocyanin. According to the results of XRD, surface modification of titanium dioxide with pigment had no effect on the crystalline phase. According to SEM results, the morphology of titanium dioxide particles is spherical structure of particles has been preserved after sensitization. At the end, the influence of the main parameters such as irradiation time, concentration of pollutant, the amount of photocatalyst and PH of solution were studied. Results showed that the removal of methylene blue using dye-sensitized titanium dioxide nanoparticles occurs under the alkaline PH condition. This study showed that the use of sensitized titanium dioxide nanoparticles is a viable option in the treatment of industrial effluents containing dye compounds.

Acknowledgments

The work is partially supported by the Islamic Azad University - Ahvaz Branch and the authors would like to thank the Research Council for their generous support of this work.

References

[1] D. Jiang, Y. Xu, D. Wu, Y. Sun, J. Solid State Chem. 181 (2008) 593–602.

[2] M. Ni, M.K.H. Leung, D.Y.C. Leung, K. Sumathy, Renew. Sustain. Energy Rev. 11 (2007) 401–425.

[3] D. Pei, J. Luan, Int. J. Photoenergy. 2012 (2012).

[4] H.R. Pouretedal, A.M. Sohrabi, J. Iran. Chem. Soc. 13 (2016) 73–79.

[5] S. Janitabar Darzi, M. Movahedi, Iran. J. Chem. Chem. Eng. 33 (2014) 55–64.

[6] P. Chowdhury, J. Moreira, H. Gomaa, A.K. Ray, Ind. Eng. Chem. Res. 51 (2012) 4523–4532.

[7] K.M. Joshi, V.S. Shrivastava, Int. J. Nano Dimens. 2 (2012) 241–252.

[8] M.A. Ahmed, E.E. El-Katori, Z.H. Gharni, J. Alloys Compd. 553 (2013) 19–29.

[9] M. Myilsamy, V. Murugesan, M. Mahalakshmi, Appl. Catal. A Gen. 492 (2015) 212–222.

[10] R. Beranek, H. Kisch, Photochem. Photobiol. Sci. 7 (2008) 40–48.

[11] J.K. Ahmed, Z.J.A. Amer, M.J.M. Al-Bahate, Int. J. Mater. Sci. Appl. 4 (2015) 21–29.

[12] Q. He, Z. Zhang, J. Xiong, Y. Xiong, H. Xiao, Opt. Mater. (Amst). 31 (2008) 380–384.

[13] M.M. Khan, S.A. Ansari, M.I. Amal, J. Lee, M.H. Cho, Nanoscale. 5 (2013) 4427–4435.

[14] P. Sivakumar, G.K.G. Kumar, S. Renganathan, J. Nanostructure Chem. 4 (2014) 107.

[15] S.R. Shirsath, D. V Pinjari, P.R. Gogate, S.H. Sonawane, A.B. Pandit, Ultrason. Sonochem. 20 (2013) 277–286.

Figure captions

Figure. 1. Anthocyanin absorption spectrum

Figure. 2. XRD patterns of pure TiO_2 and dye-modified TiO_2 samples

Figure. 3. The SEM images of TiO_2 (a), dye-modified TiO_2 (b)

Figure. 4. FT-IR spectra of (a) TiO_2, (b) Antocyanin- modified TiO_2

Figure. 5. UV–vis diffuse reflectance spectra of TiO_2 and dye-modified TiO_2.

Figure. 6. Kubelka−Munk function versus the photon energy graphs of the TiO_2 and modified TiO_2.

Figure. 7. Degradation of MB solution as a function of irradiation time (catalyst concentration 0.1 g, PH= 7 and MB concentration 10 ppm)

Figure. 8. The degradation dependence to the amount of modified TiO_2 (PH= 7 and MB concentration 10 ppm).

Figure. 9. The degradation dependence to MB initial concentration (catalyst concentration 0.1 g and PH= 7)

Figure. 10. The degradation dependence to the pH (catalyst concentration 0.1 g and MB concentration 10 ppm).

Figure. 11. The Langmuir–Hinshelwood kinetic curve for MB degradation (catalyst concentration 0.1 g, PH= 7 and MB concentration 10 ppm)

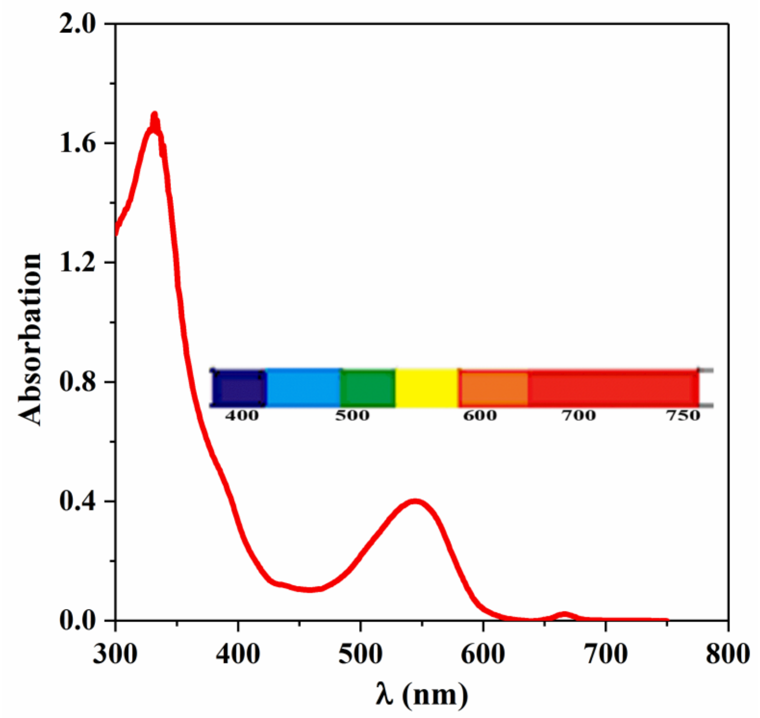
2.0
1.6
1.2
0.8
0.4
0.0
Absorbation
300
400
500
600
700
800
λ (nm)
400
500
600
700
750

Fig.1

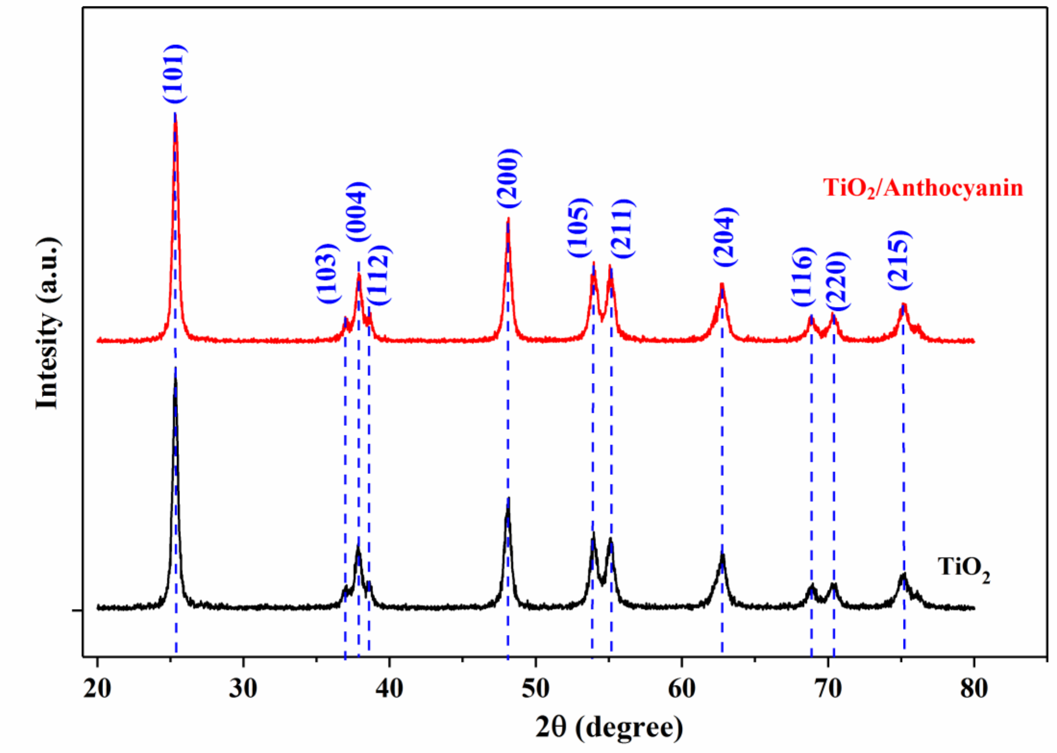
(101)
(103)
(004)
(112)
(200)
(105)
(211)
(204)
(116)
(220)
(215)
TiO2/Anthocyanin
TiO2
Intesity (a.u.)
20
30
40
50
60
70
80
2θ (degree)

Fig.2

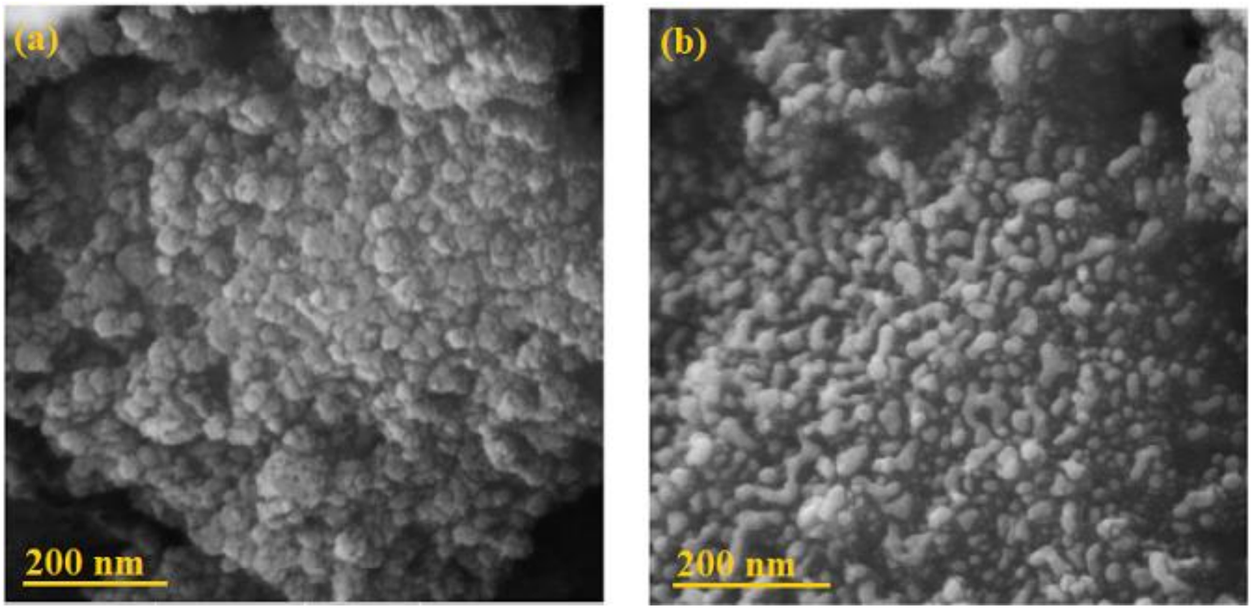
(a)
200 nm
(b)
200 nm

Fig 3.

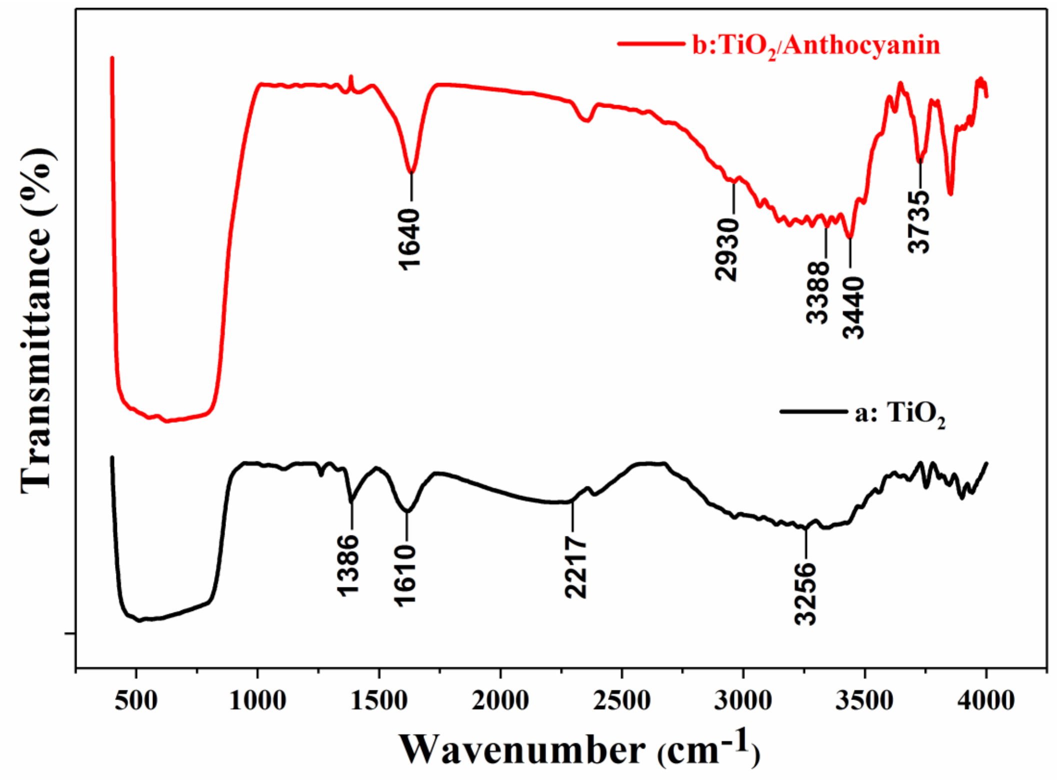
b:TiO2/Anthocyanin
a: TiO2
1640
2930
3388
3440
3735
1386
1610
2217
3256
Transmittance (%)
500
1000
1500
2000
2500
3000
3500
4000
Wavenumber (cm-1)

Fig 4.

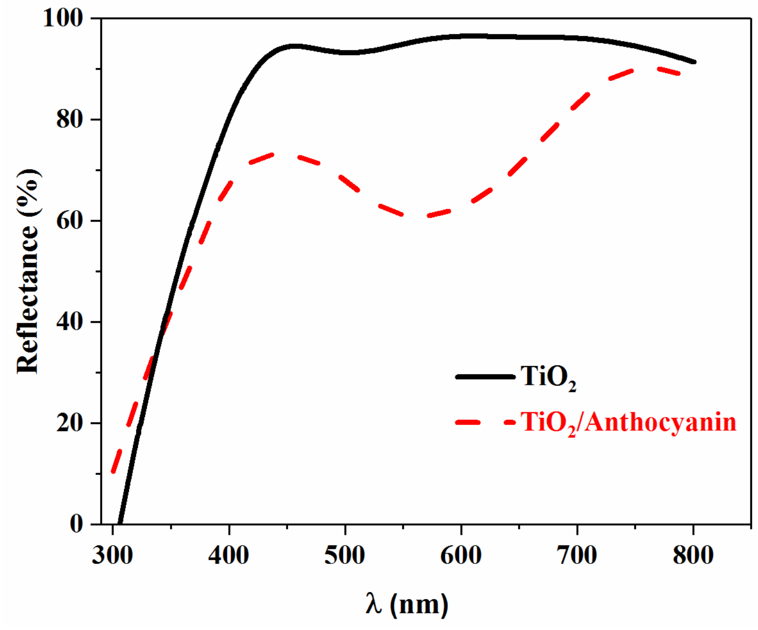
100
80
60
40
20
0
Reflectance (%)
300
400
500
600
700
800
λ (nm)
TiO2
TiO2/Anthocyanin

Fig 5.

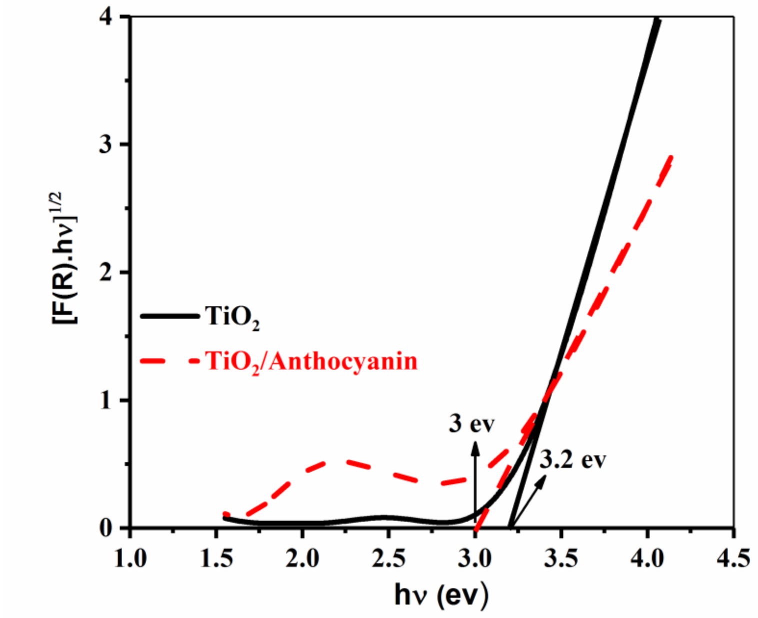

Fig 6.

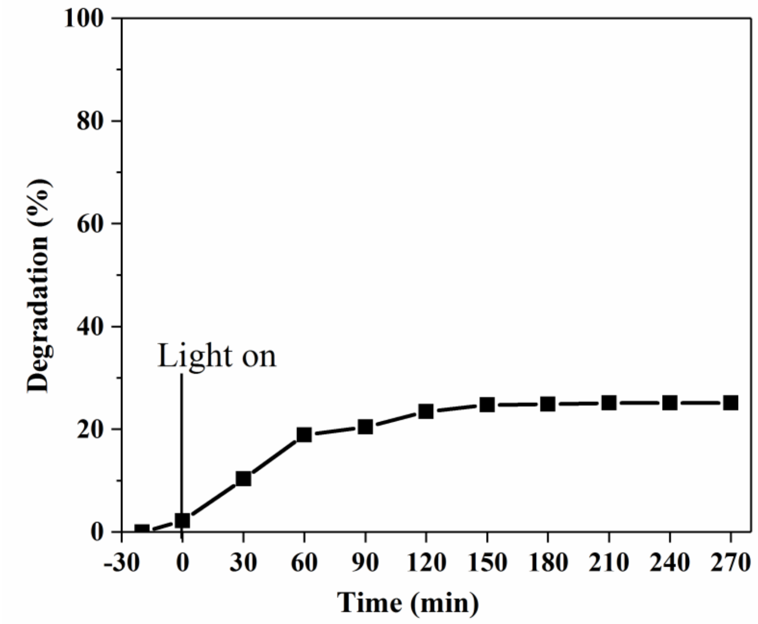

Fig 7.

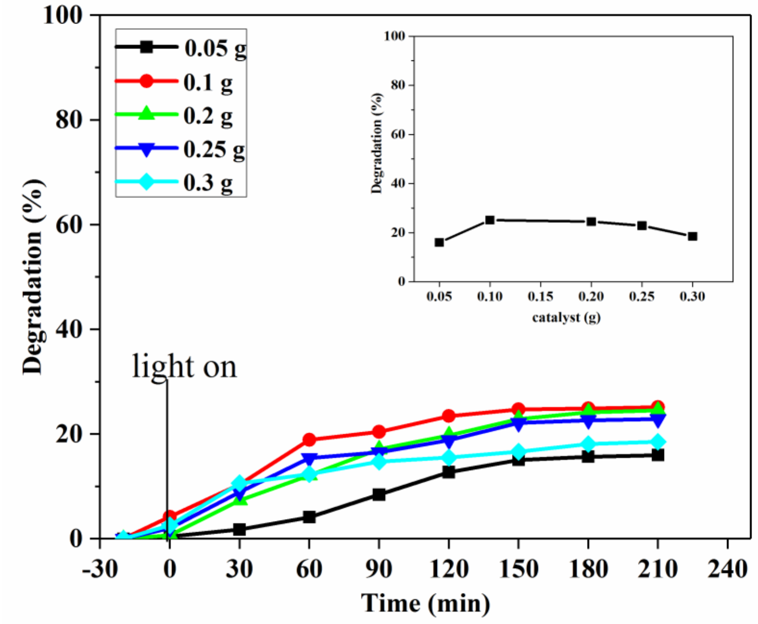
0.05 g
0.1 g
0.2 g
0.25 g
0.3 g
light on
Degradation (%)
Time (min)
Degradation (%)
catalyst (g)

Fig 8.

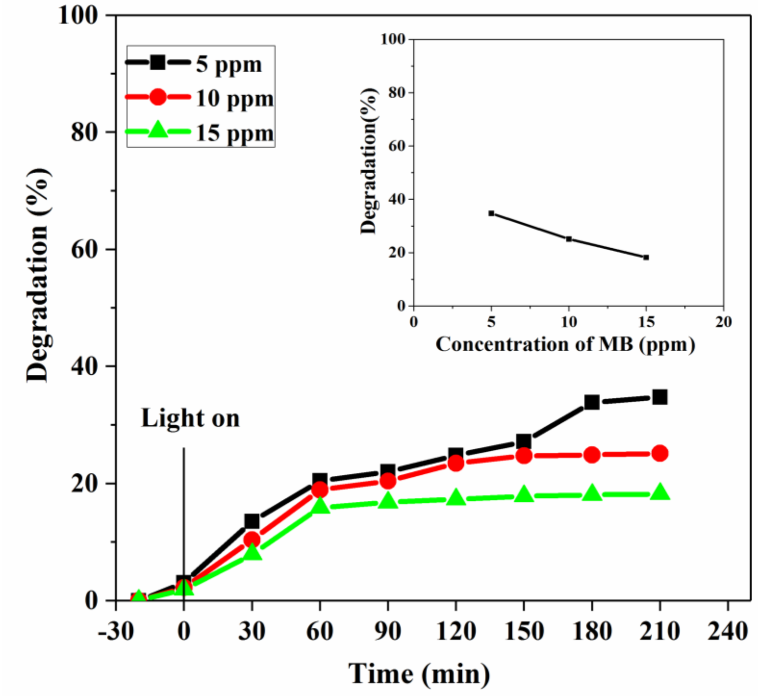
5 ppm
10 ppm
15 ppm
Light on
Degradation (%)
Time (min)
Degradation(%)
Concentration of MB (ppm)

Fig 9.

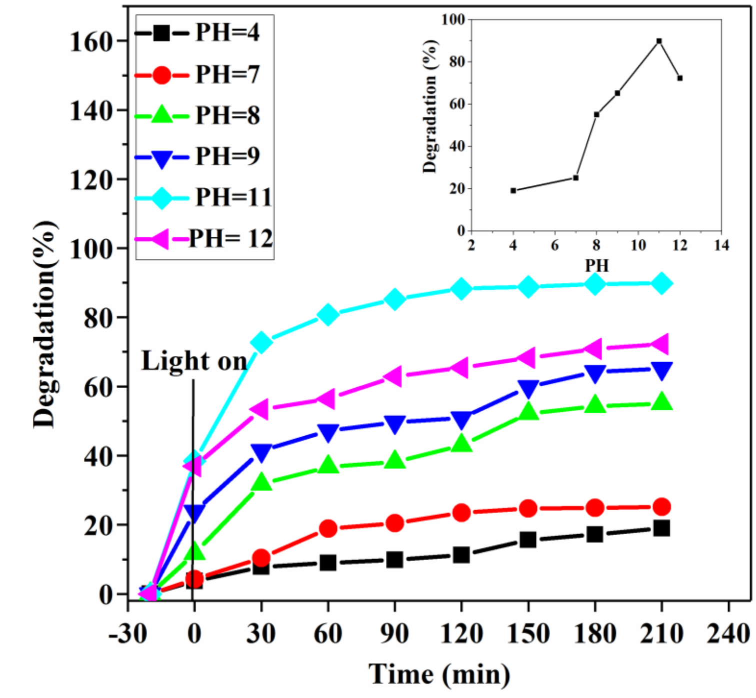
PH=4
PH=7
PH=8
PH=9
PH=11
PH= 12
Light on
Degradation(%)
0
20
40
60
80
100
120
140
160
-30
0
30
60
90
120
150
180
210
240
Time (min)
Degradation (%)
PH
2
4
6
8
10
12
14

Fig 10.

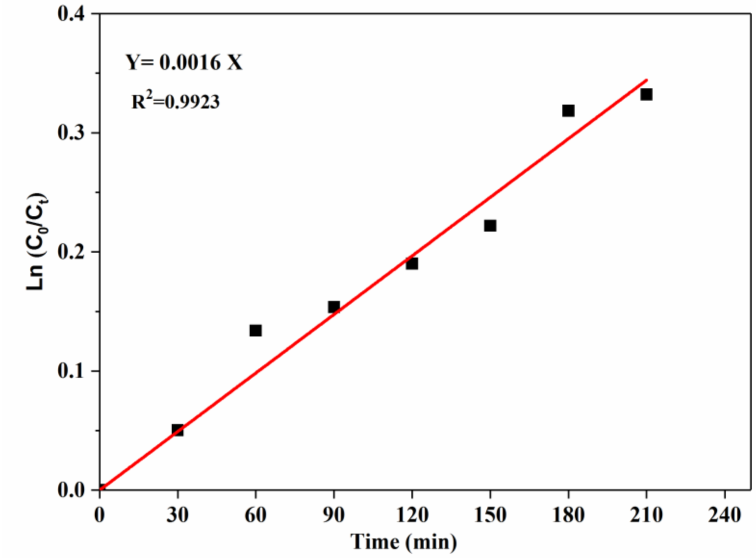
Y= 0.0016 X
R²=0.9923
Ln (C0/Ct)
0.0
0.1
0.2
0.3
0.4
0
30
60
90
120
150
180
210
240
Time (min)

Fig 11.