

## Combined effect of adsorbent chitosan and photosensitizer polypyrrole in ternary chitosan-polypyrrole-TiO<sub>2</sub> photocatalyst leading to visible light activity and superior functionality

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Received 25 March 2016; revised and accepted 23 February 2017

The combined effect of the components in the ternary chitosan-polypyrrole-TiO<sub>2</sub> (Chit-Ppy-TiO<sub>2</sub>) photocatalytic system has been investigated. The role of each component in this catalyst is validated by the visible light degradation of the model dye methylene blue. The reaction parameters, viz., amount of catalyst, dye concentration, oxidant concentration and temperature are studied in detail. The ternary system exhibits greater activity when compared to both the single and binary component catalysts (chitosan-TiO<sub>2</sub> and polypyrrole-TiO<sub>2</sub>). The superior functionality of Chit-Ppy-TiO<sub>2</sub> (1:1:100 wt ratio) originates from the combined effect of greater dye adsorption of chitosan, visible light sensitization of polypyrrole and the catalytic functionality of TiO<sub>2</sub>. The ternary photocatalyst is recyclable even after fourth run without appreciable loss in its activity.

**Keywords:** Catalysts, Ternary catalysts, Chitosan-polypyrrole-titania, Polypyrrole, Titania, Photodegradation, Dye degradation, Visible light photodegradation, Methylene blue

TiO<sub>2</sub> is an attractive semiconductor material for photocatalysis due to its low cost, high photocatalytic activity, stability in aqueous systems and low environmental toxicity<sup>1</sup>, to degrade organic pollutants under ultraviolet irradiation<sup>2,3</sup>. However, the application of TiO<sub>2</sub> is limited under visible light due to its wide band gap ( $E_g = 3.2$  eV) and high recombination rate of photogenerated electrons and holes<sup>4-7</sup>. Thus, degradation of organic pollutants and dyes present in the industrial wastewater using TiO<sub>2</sub> semiconductor photocatalyst remains a challenge particularly under visible/solar light. Modifications are, therefore, made to convert UV active TiO<sub>2</sub> into visible light active photocatalyst. The effects of metal and non-metal ion as dopant such as Ag, Fe, Pt, C, N and S were investigated to overcome the practical limitations of TiO<sub>2</sub><sup>5-8</sup>. Alternatively, co-doping with two kinds of heteroelements or co-modification with two kinds of nanoparticles or organic dyes of a semiconductor photocatalyst (i.e. a ternary system) has been studied and has provided better photocatalytic performance of the catalyst as a result of the improved charge separation efficiency and the broadening of light absorption spectra, and so on<sup>9</sup>. We recently reported

the synthesis, characterization and a preliminary level assessment of photocatalytic activity of a novel ternary photocatalyst consisting of chitosan, polypyrrole and TiO<sub>2</sub> with methylene blue (MB) dye degradation<sup>10</sup>.

Methylene blue (MB) is a basic dye, extensively used for dyeing and printing cotton, wool and silk fibres. The dye when present in effluent can cause harmful effects such as eye burns, nausea, vomiting, etc., in human being<sup>11</sup>. It is also widely studied as a model dye in many photocatalytic degradation experiments. Hence, MB was chosen as the model dye in our previous work to test the photocatalyst, Chit-Ppy-TiO<sub>2</sub><sup>10</sup>. It was found that the dye degradation activity was in the increasing order: single < binary < ternary. The ternary system had very high activity compared to single/pristine TiO<sub>2</sub>. For an understanding as to how this activity is enhanced in the ternary catalyst, a thorough investigation of its catalytic behaviour is needed. This is also essential for its potential applications. Hence, the present work is focussed on a systematic investigation of its physico-chemical characteristics and its catalytic functionality. The degradation reaction is investigated by varying the reaction parameters like amount of catalyst, dye concentration, amount of H<sub>2</sub>O<sub>2</sub>, pH of the solution etc. The results show that each component in the ternary system contributes and plays an important role in deciding the ultimate high activity of the catalyst.

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### Materials and Methods

A series of ternary photocatalysts of chitosan–polypyrrole–TiO<sub>2</sub> (Chit-Ppy-TiO<sub>2</sub>) with different component weight proportions (1:1:1, 1:1:5, 1:1:10, 1:1:20, 1:1:50, 1:1:100 and 1:1:200) were synthesized (Supplementary Data) and characterized as per our earlier report<sup>10</sup>. However, photo images (in order to realize their colours and the consequent visible light absorption) and surface area characterizations are reported herein. The still photographs of the catalyst samples were taken with a Sony Cyber-shot digital camera. Surface area of the photocatalysts was analyzed with Micromeritics ASAP 2020 using N<sub>2</sub> adsorption technique at 77K. LC-MS spectral data of the MB degraded products were obtained with Micromass Q-TOF-micro instrument.

### Photocatalysis experiments

The experimental method followed in the preliminary study<sup>10</sup> was adopted in the present study also (Supplementary Data). The pH of the initial dye

solution was adjusted with 0.1 M NaOH and 0.1 M HCl during the pH variation parametric study. Then, 5 mL of borate buffer was added to make the dye solution pH to 9.2. Solar degradation reaction was carried out with the selected catalysts Chit-Ppy-TiO<sub>2</sub> (1:1:100) and TiO<sub>2</sub> using a beaker as a reactor, mimicking the natural condition of dye effluent exposure to sunlight. A set of four reactions was carried out simultaneously at 11 am to 1 pm of a sunny day to avoid any error due to change of solar intensity and incident angle of the sunlight.

### Results and Discussion

#### Characterization of the photocatalysts

For a clear vision of the color of the ternary photocatalysts, photographs of the samples were taken and are shown in Fig. 1. The results clearly distinguish the ternary catalysts from the original individual components. The gradual increase of Ppy weight proportion in the ternary catalysts from (1:1:100) to (1:1:1) (i.e. TiO<sub>2</sub> content decreases while

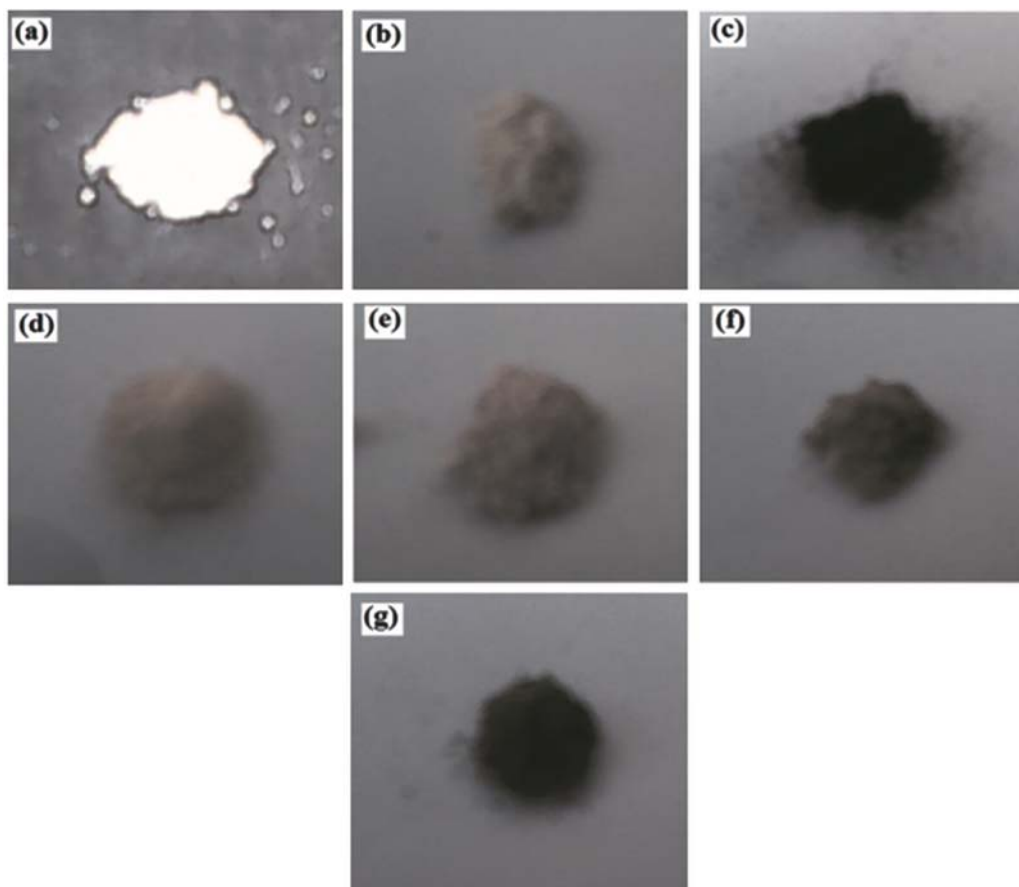


Fig. 1 — Images of (a) TiO<sub>2</sub>, (b) Chit, (c) Ppy, (d) Chit-Ppy-TiO<sub>2</sub> (1:1:100), (e) Chit-Ppy-TiO<sub>2</sub> (1:1:50), (f) Chit-Ppy-TiO<sub>2</sub> (1:1:10) and (g) Chit-Ppy-TiO<sub>2</sub> (1:1:1).

Ppy content increases in the above series) gradually intensifies the darkness of the ternary system photocatalysts (Fig. 1, images d–g). Correspondingly, their absorption in the visible region could also gradually increase.

The anatase TiO<sub>2</sub> exhibits a typical type-IV isotherm (Fig. S1) with BET N<sub>2</sub> adsorption (Brunauer-Emmett-Teller) and has a surface area of 8.7 m<sup>2</sup>/g (Table 1). The nature of isotherm is retained in ternary catalysts also (Supplementary Data, Fig. S1). However, the surface area of pristine TiO<sub>2</sub> is reduced to 3.63 m<sup>2</sup>/g in Chit-Ppy-TiO<sub>2</sub> (1:1:1), and increased to 12.38 m<sup>2</sup>/g in Chit-Ppy-TiO<sub>2</sub> (1:1:100). This reveals that as the polymer content in the ternary catalyst is reduced, the surface area is increased.

#### Photocatalytic degradation of MB dye

The data given in Table 2 give the 1 h and 2 h visible light degradation efficiency (in %) of different catalysts. MB dye being colored, undergoes self degradation even in the absence of any catalyst and H<sub>2</sub>O<sub>2</sub> to an extent of 14.1% in 2 h duration. However, the supply of H<sub>2</sub>O<sub>2</sub> almost doubles the self degradation of MB both in 1 h and 2 h duration and therefore most of the reactions were performed in the presence of H<sub>2</sub>O<sub>2</sub>. Values in Table 2 also reveal that the ternary system exhibits higher efficiency than their binary counterparts Chit-TiO<sub>2</sub> and Ppy-TiO<sub>2</sub> and far higher efficiency than their single counterparts (Chit, Ppy, TiO<sub>2</sub>) under similar condition.

The degradation of MB dye through its visible spectral changes was studied and the spectral changes of MB observed during its degradation with the catalyst Chit-Ppy-TiO<sub>2</sub> (1:1:100) are shown in Fig. S2 (Supplementary Data). Absorbance of the dye decreases with increase in reaction time showing the dye degradation. It is noted that the position of absorption maximum gets shifted toward lower wavelength side. This is attributed to the removal of methyl groups from MB via N-dealkylation<sup>11</sup>.

Bare TiO<sub>2</sub> exhibits 58.6% degradation efficiency in 1 h in the presence of H<sub>2</sub>O<sub>2</sub> but only low value (11.3%) without H<sub>2</sub>O<sub>2</sub> (Table 2). This low value is quite consistent with the phenomenon of UV-absorbing nature of TiO<sub>2</sub> ( $\lambda \leq 380$  nm) and the availability of feeble intensity of light in the wavelength region  $\lambda = 380$ –400 nm from 150W tungsten-halogen lamp. The higher activity of TiO<sub>2</sub> with H<sub>2</sub>O<sub>2</sub> under visible light irradiation is remarkable, though reported in an earlier review paper<sup>12</sup>. This phenomenon has been explained by the photo-induced ligand to metal charge

transfer (LMCT) complex formation between TiO<sub>2</sub> and the TiO<sub>2</sub>-adsorbate H<sub>2</sub>O<sub>2</sub> (the H<sub>2</sub>O<sub>2</sub> exists in the coordinated form with TiO<sub>2</sub>) through their interaction under irradiation<sup>12</sup>. In the excited state configuration, the complex absorbs light and leads to the production of hydroxyl radicals (OH<sup>•</sup>) which become responsible for MB degradation<sup>12</sup>.

Figure 2 illustrates a graphical profile of the degradation efficiencies of ternary catalysts in a systematic variation. The degradation efficiency of the ternary system increases with increase in TiO<sub>2</sub> content, reaches maximum at 1:1:100 and decreases beyond 1:1:100. Therefore, 1:1:100 of Chit-Ppy-TiO<sub>2</sub> is the optimal weight proportion of the three components. It is also notable that the efficiency is reduced to 34.6% for the ternary system with equal proportion of the three components (1:1:1). This is attributed to the decrease in exposure of active sites of TiO<sub>2</sub> in the ternary system, as supported by the decrease in surface area and pore volume of this catalyst in BET N<sub>2</sub> adsorption/desorption experiment (Table 1, Supplementary Data, Fig. S1).

To get an insight in to the contributory role of chitin and polypyrrole components in the optimized

Table 1 — Surface area data of the photocatalysts

Sample	Surface area <sup>a</sup> (m <sup>2</sup> /g)	Pore vol. <sup>b</sup> × 10 <sup>-2</sup> (cm <sup>3</sup> /g)
TiO <sub>2</sub>	8.70	3.87
Chit-Ppy-TiO <sub>2</sub> (1:1:1)	3.63	1.48
Chit-Ppy-TiO <sub>2</sub> (1:1:10)	9.86	3.14
Chit-Ppy-TiO <sub>2</sub> (1:1:100)	12.38	3.27

<sup>a</sup>BET method; <sup>b</sup>Single point pore volume

Table 2 — Visible light degradation of MB over single, binary and ternary catalysts. [Reaction cond.: [MB] = 50 mg/L (200 mL), catalyst amt = 500 mg/L, H<sub>2</sub>O<sub>2</sub> = 10 mL/L, pH = 6.9]

Catalyst	MB degrad. (%) in		Ads. capacity (mg/g <sub>cat</sub> )
	1 h	2 h	
Self-degradation	14.2 (7.7) <sup>a</sup>	26.9 (14.1) <sup>a</sup>	–
TiO <sub>2</sub>	58.6 (11.3) <sup>a</sup>	82.5 (17.7) <sup>a</sup>	3.8
Chit	10.3	15.2	7.2
Ppy	7.2	16.0	3.2
Chit-TiO <sub>2</sub> (1:100)	67.2	89.2	5.0
Ppy-TiO <sub>2</sub> (1:100)	72.8	93.8	3.4
Chit-Ppy-TiO <sub>2</sub> (1:1:100)	86.4	98.9	4.6
Chit-Ppy-TiO <sub>2</sub> (1:1:200)	71.2	94.2	4.2

<sup>a</sup>In the absence of H<sub>2</sub>O<sub>2</sub>.

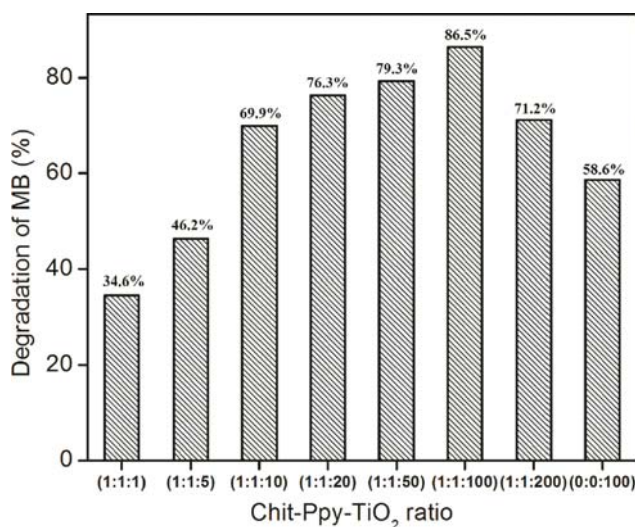


Fig. 2 — Effect of components weight ratio of ternary catalyst system on the visible light degradation of MB. [Reaction cond.: [MB] = 50 mg/L (200 mL); catalyst amt = 500 mg/L; H<sub>2</sub>O<sub>2</sub> = 10 mL/L; pH = 6.9; Time = 1 h.

ternary catalyst (1:1:100), adsorption experiment was carried out and the results are given in Table 2. Chitosan with the highest adsorption capacity, adsorbs more dye molecules than other materials and this is consistent with the established fact that chitosan is a good adsorbent<sup>13</sup>. Therefore, when chitosan is coupled with TiO<sub>2</sub> either separately or with Ppy, it improves the adsorption capacity of resulting binary or ternary catalyst respectively. Consequently, chit is able to supply adsorbed dye molecules continuously to the active sites of catalyst which inhibits e<sup>-</sup>-h<sup>+</sup> recombination in TiO<sub>2</sub><sup>14</sup>. Ppy sensitizes TiO<sub>2</sub> with more quantum of visible light absorption (brownish of white TiO<sub>2</sub> as deduced from the photo image of Fig. 1d) which enhances the extent of degradation of the adsorbed dye molecules<sup>15</sup>. Thus, combined effect operates efficiently among all the three components in the ternary system Chit-Ppy-TiO<sub>2</sub> at the weight ratio of 1:1:100, which ultimately brings about the observed high efficiency.

#### Effect of reaction constituents on the degradation of MB dye

The study of reaction constituents and parameters provides an insight into the MB degradation reaction. The catalyst, Chit-Ppy-TiO<sub>2</sub> (1:1:100) exhibiting the greatest activity was considered for evaluating the effect of reaction constituents and the obtained results are plotted in Fig. 3. The degradation efficiency is very low (5.4%) in the absence of light (Cat+H<sub>2</sub>O<sub>2</sub> only) but increases with high impact (91.2%) upon

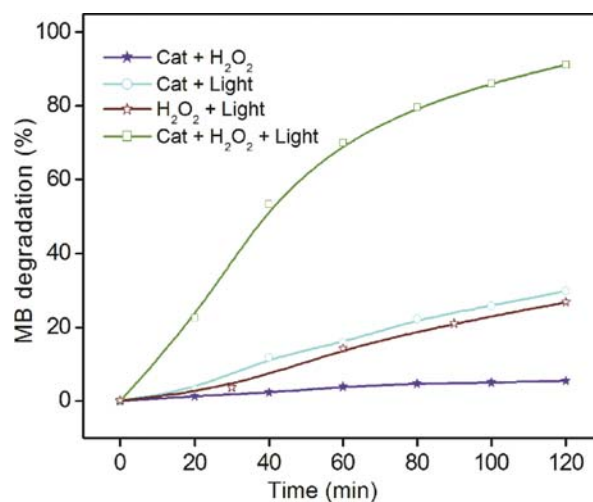


Fig. 3 — Effect of reaction constituents on the degradation of MB with Chit-Ppy-TiO<sub>2</sub> (1:1:100) catalyst.

supplying light energy (Cat+H<sub>2</sub>O<sub>2</sub>+light). At the same time, the degradation reaches only 26.9% in the absence of catalyst (H<sub>2</sub>O<sub>2</sub>+light) and 30% in the absence of H<sub>2</sub>O<sub>2</sub> (Cat+light). These results unequivocally demonstrate that all the three constituents, catalyst, light and H<sub>2</sub>O<sub>2</sub>, are required for maximum degradation of MB dye. The results further substantiate the involvement of two excitation processes in the presence of light energy, viz., dye sensitized excitation and catalyst-H<sub>2</sub>O<sub>2</sub> complex mediated excitation (will be discussed under mechanism of degradation).

#### Effect of reaction parameters on degradation of MB dye

The surface of the heterogeneous catalyst, which favors more adsorption of reactant, results in more degradation<sup>16</sup>. The optimized catalyst Chit-Ppy-TiO<sub>2</sub> (1:1:100) was employed for optimization of various other reaction parameters. The results are given in Fig. 4. Firstly, with regard to catalyst dose, the catalyst amount upto 250 mg/L increases the degradation % of MB appreciably and above this dose it shows only a small effect (Fig. 4a) and therefore 250 mg/L is the optimal catalyst dose. At this dose, the number of exposed active sites on the surface becomes almost constant. However, above this catalyst amount, the light particles get scattered with decreased penetration and this condition reduces the dye degradation level<sup>17,18</sup>.

The second parameter is the volume of H<sub>2</sub>O<sub>2</sub> and its influence on degradation (Fig. 4b). As observed already, the presence of H<sub>2</sub>O<sub>2</sub> in the reaction mixture facilitates the degradation of MB. The % degradation

is enhanced with increase in volume of H<sub>2</sub>O<sub>2</sub> used but it is levelled at 10 mL/L. At the H<sub>2</sub>O<sub>2</sub> volume of 20 mL/L, the increase in % degradation of MB is not appreciable and therefore 10 mL/L is the optimal H<sub>2</sub>O<sub>2</sub> volume.

The change in initial concentration of MB has greater impact on its % degradation (Fig. 4c). At the lowest MB concentration (10 mg/L), the degradation attains maxima, i.e., complete degradation in less than 30 min. At 25 and 40 mg/L MB concentrations also, the degradation is complete, i.e., 100%. Further increase in [MB] decreases the % degradation of MB and this is attributed to the progressive decrease in amount of dye molecule adsorption on the fixed quantity of photocatalyst<sup>19</sup>. For first three concentrations, 10, 25 and 40 mg/L, the dye gets complete degradation within/at 2 h. For higher concentrations, the amount of dye degradation (in mg/L in 2 h) is 48.25 for 50 mg/L, 69.56 for 75 mg/L and 83.59 for 100 mg/L. Although there is a decrease in % degradation with increase in dye concentration (Fig. 4c) it is different in terms of concentration. As the initial concentration is

increased, the amount of MB degraded is also increased. At fixed catalyst dose (250 mg/L), the amount of dye molecule adsorption on catalyst may go down with increase in initial dye concentration. However, the observed enhancement in amount of dye degradation may have the origin in the following phenomena reported in previous works<sup>20,21</sup>. Colored dye molecules in principle can improve the activity of catalyst via dye sensitization. In addition, it inhibits recombination of e<sup>-</sup>-h<sup>+</sup> pair by increasing the charge separation and thus increases the efficiency of the photocatalytic process. Thus, it also increases the spectrum response range.

The pH of the reaction medium has a great influence on the degradation of MB. The data plotted in Fig. 4d clearly demonstrate the effect of H<sup>+</sup> and OH<sup>-</sup> ions in creating the active sites of the catalyst and on MB degradation. The natural pH (6.9) provides very feebly charged catalyst surface (pH<sub>zpc</sub> of ternary catalyst = 7.2) and results in higher degradation efficiency as compared to alkaline pH. However, acidic pH 4.0 also favours higher degradation. Olajire *et al.*<sup>22</sup> have reported a similar type of H<sup>+</sup> dependent reaction in their study.

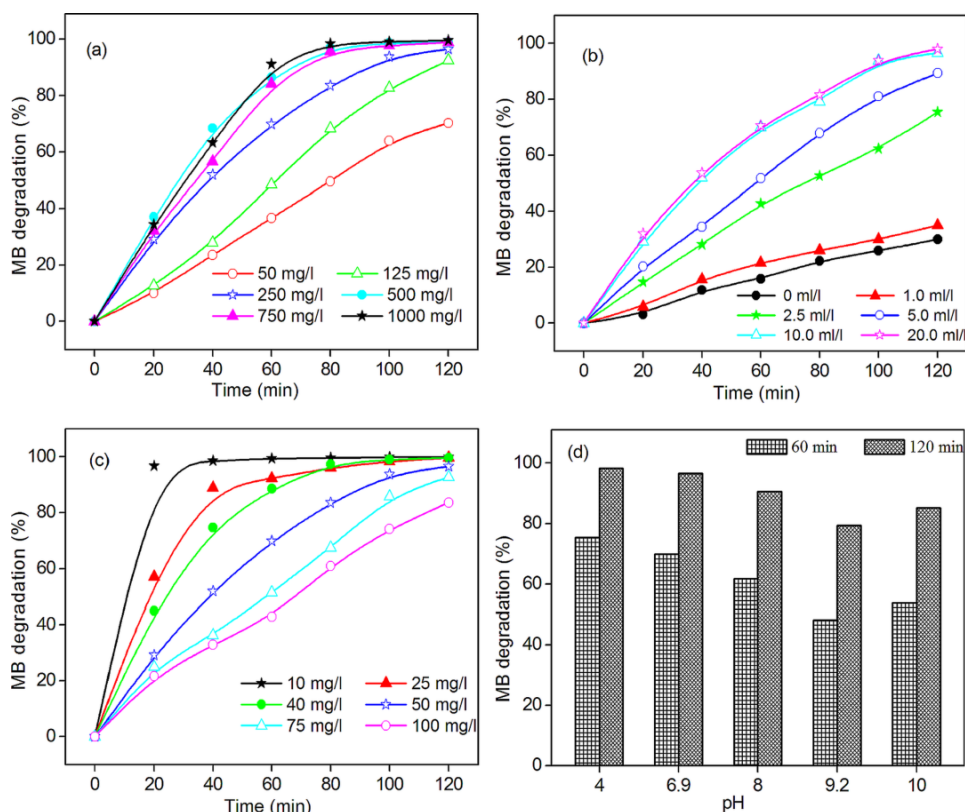


Fig. 4 — Effect of reaction parameters (a) catalyst amount, (b) H<sub>2</sub>O<sub>2</sub> amount, (c) [MB] and (d) pH on Chit-Ppy-TiO<sub>2</sub> (1:1:100) catalysed visible light MB degradation. [Common reaction cond.: catalyst amt = 250 mg/L, H<sub>2</sub>O<sub>2</sub> = 10 mL/L, [MB] = 50 mg/L, pH = 6.9, Temp. = 25 °C.



This trend indicates that the dye molecules are highly susceptible to attack by the  $\text{OH}^\bullet$  radicals in acidic medium. The increase in pH may increase the rate of  $e^- - h^+$  recombination<sup>23</sup>. At pH 9.2, the presence of borate buffer ions provides some sort of inhibition to the mobility of dye molecules during the adsorption step. This delays the adsorption process which is followed by lowering in the degradation of MB.

#### Reusability of the ternary photocatalyst

Efficiency and physico-chemical stability of the optimized catalyst Chit-Ppy-TiO<sub>2</sub> (1:1:100) on reuse were investigated. The catalyst was separated from the reaction solution via simple filtration, washed thoroughly with water, dried in air oven at 80°C for 2 h and then used for subsequent reactions. The catalyst exhibits 96.5, 96.2, 95.8 and 94.3% degradation efficiencies in four successive catalytic runs (Fig. 5). This clearly demonstrates the reusability and sustainability of the catalyst. Almost a constant efficiency in degradation of MB (96.5% in fresh form and 94.3% in fourth cycle) is maintained during four cycles of experiments.

#### Solar degradation of MB: A comparison between TiO<sub>2</sub> and Chit-Ppy-TiO<sub>2</sub> (1:1:100)

A primary attempt was made to evaluate the catalytic efficiencies of bare TiO<sub>2</sub> and Chit-Ppy-TiO<sub>2</sub> (1:1:100) in the presence of natural renewable solar light. The results are given in Table 3. It is noted that the self-degradation of the dye is increased from 14.1% to 20.96% by the use of sun light in comparison to the visible light (150 W) from tungsten lamp. This may be attributed to the presence of 5% of UVC rays ( $\lambda \geq 350$  nm) in the natural sun light. The presence of TiO<sub>2</sub> catalyst (without H<sub>2</sub>O<sub>2</sub>) in the

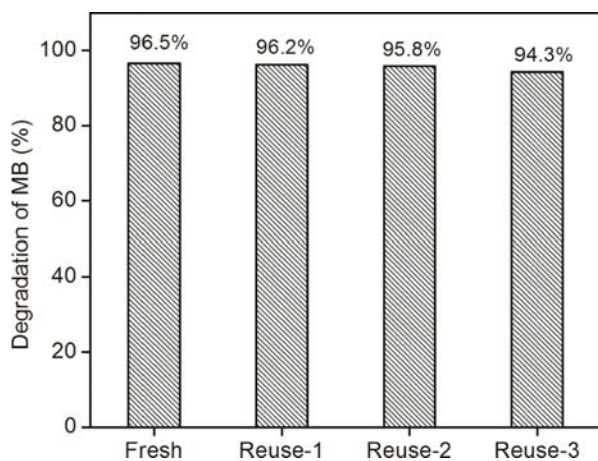


Fig. 5 — Reusability of the ternary photocatalyst.

reaction medium enhances the self-degradation of the dye slightly (from 20.96% to 28.95%). However, the presence of ternary catalyst decreased the self degradation perhaps through adsorption process. Also, this is attributed to the absorption of sun light by the ternary catalyst which in turn reduces the availability of light energy to the dye molecules.

These results observed in the presence of catalyst (TiO<sub>2</sub>/ternary catalyst) but without H<sub>2</sub>O<sub>2</sub> are dramatically modified when H<sub>2</sub>O<sub>2</sub> was added to the reaction medium. The efficiency of TiO<sub>2</sub> is increased enormously, almost by 3 times while the ternary catalyst has completely degraded the dye molecules. It is interesting to note that even with sunlight the efficiency of ternary catalyst (99.6%) is greater than that of bare TiO<sub>2</sub> (81.3%). In both cases, thus, the efficiencies of the catalysts are definitely higher in sunlight than in laboratory visible light. This greater enhancement in % of degradation with H<sub>2</sub>O<sub>2</sub> is certainly due to its behaviour to release  $\text{OH}^\bullet$  radicals. This and the earlier observation (Table 2) together prove that ternary catalyst with Chit and Ppy loading over TiO<sub>2</sub> (1:1:100) is certainly more efficient than bare TiO<sub>2</sub>. That means the ternary catalyst designed, synthesized and investigated in the present work can function as an efficient photocatalyst both in lab-available visible light and the naturally available sunlight.

#### Plausible degradation mechanism of MB

The photodegradation mechanism with H<sub>2</sub>O<sub>2</sub> in the presence of TiO<sub>2</sub>/solid ternary catalyst follows a classical adsorption-oxidation-desorption type mechanism as discussed by Zhang *et al.*<sup>24</sup> with MnO<sub>2</sub>. The excitation of valence electrons to the conduction band takes place via three major processes, as depicted in Fig. 6.

MB being colored, undergoes excitation in the visible region and involves in the formation of  $\text{OH}^\bullet$  radicals from H<sub>2</sub>O<sub>2</sub> as given in Fig. 6a. TiO<sub>2</sub> in the form of TiO<sub>2</sub>-H<sub>2</sub>O<sub>2</sub> complex absorbs visible light, undergoes

Table 3 — Solar degradation of MB over TiO<sub>2</sub> and Chit-Ppy-TiO<sub>2</sub> (1:1:100). [Catalyst amt = 250 mg/L, MB = 50 mg/L, Time = 2 h, H<sub>2</sub>O<sub>2</sub> = 10 mL/L]

Catalytic cond.	MB degrad. (%) in	
	Visible light	Sunlight
Self-degradation (without H <sub>2</sub> O <sub>2</sub> )	14.1	20.96
TiO <sub>2</sub> (without H <sub>2</sub> O <sub>2</sub> )	13.6	28.95
Chit-Ppy-TiO <sub>2</sub> (1:1:100) (without H <sub>2</sub> O <sub>2</sub> )	30.0	11.5
TiO <sub>2</sub> (with H <sub>2</sub> O <sub>2</sub> )	67.2	81.3
Chit-Ppy-TiO <sub>2</sub> (1:1:100) (with H <sub>2</sub> O <sub>2</sub> )	96.5	99.6

<sup>a</sup>Light intensity from sunlight = 18.19 mW/cm<sup>2</sup>; <sup>b</sup>from visible light = 14.83 mW/cm<sup>2</sup>.

excitation of electron from the valence band to the conduction band and produces OH<sup>•</sup> radicals<sup>12</sup> as shown in Fig. 6b. Chit thin layer present in the ternary photocatalyst provides adsorptive sites to the dye molecules. A thin layer of Ppy absorbs visible light, undergoes  $\pi-\pi^*$  electronic transition and transfers its photogenerated electron ( $e^-$ ) into the conduction band of TiO<sub>2</sub><sup>25</sup>. In addition, Ppy is assumed to collect photogenerated holes and to channelize them into the polymer/solution interface promoting effective charge carrier separation<sup>26</sup>. Thus, the ternary catalyst provides adsorption sites both to dye molecules and to H<sub>2</sub>O<sub>2</sub> on its surface. This inhibits surface recombination of  $e^-h^+$  pair that is usually encountered with TiO<sub>2</sub><sup>4-7,27</sup>.

The plausible mechanism follows the steps similar to the one reported with MnO<sub>2</sub><sup>24</sup> and ZnO<sup>28</sup>. Upon exposure to visible light, the adsorbed dye molecule absorbs light energy, gets excited ( $D_{ads}^*$ ) and injects its

electron into the conduction band of TiO<sub>2</sub> catalyst. O<sub>2</sub>/H<sub>2</sub>O<sub>2</sub> traps electrons from the surface and undergoes decomposition with the production of O<sub>2</sub><sup>-•</sup>/OH<sup>•</sup> radicals (Eq. 1 – 6). These species attack MB and decompose it. MB<sup>•+</sup> produced after losing  $e^-$  to TiO<sub>2</sub> may also undergo self-degradation. In the case of TiO<sub>2</sub>-H<sub>2</sub>O<sub>2</sub> complex, H<sub>2</sub>O<sub>2</sub> accepts a photogenerated electron from TiO<sub>2</sub> conduction band and catalytically produces free radical species such as HO<sup>•</sup>, HOO<sup>•</sup> or O<sub>2</sub><sup>-•</sup> according to Eqs. 3–6 promoting the charge separation<sup>28</sup>. These free radicals cause the oxidative destruction of MB (Eq. 7). The excited  $e^-$  transfer from Ppy to TiO<sub>2</sub> is followed by the formation of OH<sup>•</sup> radicals as described in Fig. 6c leaving Ppy<sup>+</sup>. Ppy<sup>+</sup> may get regeneration to Ppy by reaction with ground/excited MB, (eqn. 8), which, in turn, promotes MB degradation. Ppy<sup>+</sup> may also react with H<sub>2</sub>O<sub>2</sub> producing Ppy and other H<sub>2</sub>O<sub>2</sub> decomposed species.

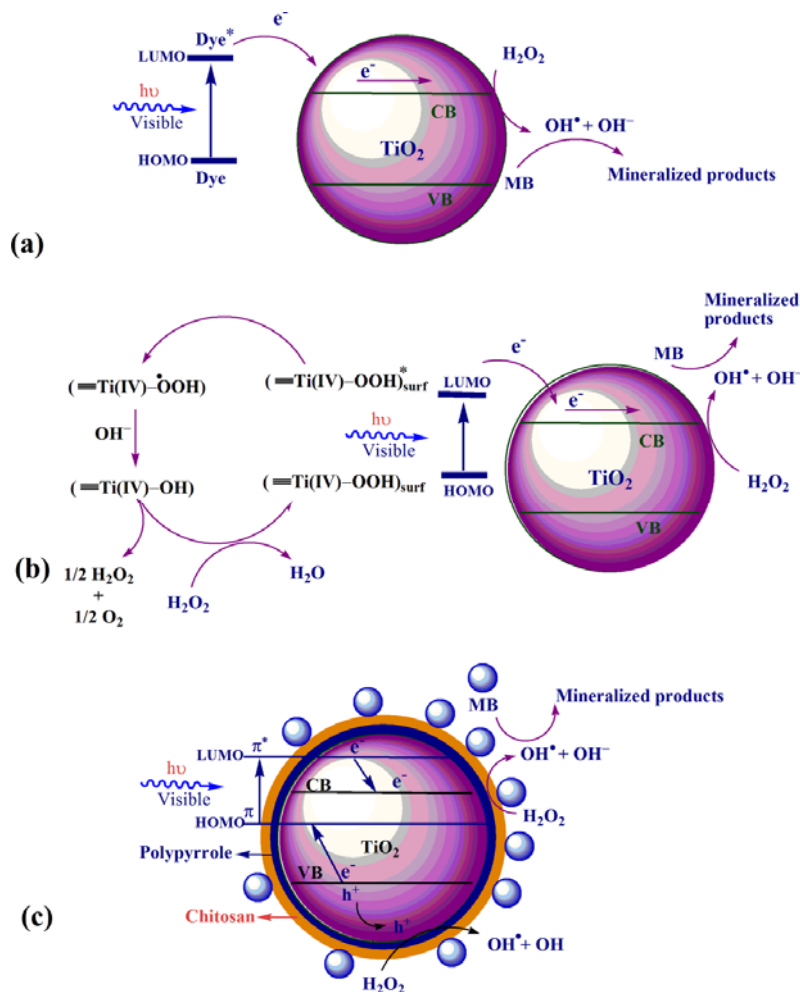
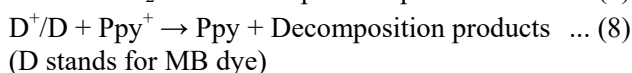
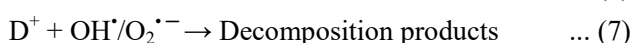
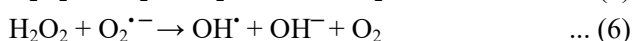
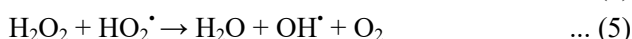
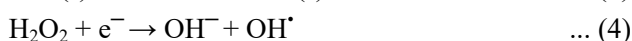
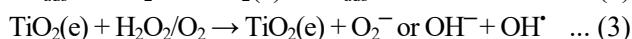
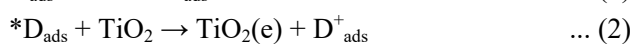


Fig. 6 — Mechanism of visible light photodegradation of MB via (a) MB sensitized TiO<sub>2</sub>, (b) TiO<sub>2</sub>-H<sub>2</sub>O<sub>2</sub> complex sensitized TiO<sub>2</sub> and (c) Chit-Ppy-TiO<sub>2</sub> mediation.

It is important to note that the decomposition of  $\text{H}_2\text{O}_2$  does not take place in the absence of light and only the available  $\text{O}_2^{\cdot-}$  (aeration of the solution through bubbling) causes the decomposition of MB in the absence of  $\text{H}_2\text{O}_2/\text{H}_2\text{O}_2$  without light at the meagre level. Also the degradation efficiency in the absence of catalyst is very less due to the unavailability of adsorption sites and redox species like  $e^-$  or  $h^+$ . The degraded products desorb from the catalyst surface to regenerate the active sites of the catalyst.



In summary, Ppy as a sensitizer excites and injects  $e^-$  to CB of  $\text{TiO}_2$ . The hole in  $\text{Ppy}^+$  produces  $\text{OH}^{\cdot}$  with  $\text{H}_2\text{O}_2$  and then Ppy regenerates. Chit adsorbs MB and facilitates  $\text{MB}^+$  formation by reacting with  $h^+$ . Thus,  $e^- - h^+$  pair separation becomes easier. Chit and Ppy work together and exhibit a combined effect. The presence of chitosan in the catalyst favours the adsorption of both dye and  $\text{H}_2\text{O}_2$  and the Ppy favours easier transfer of conduction band electron into  $\text{H}_2\text{O}_2$  molecule. Excess  $\text{H}_2\text{O}_2$  may act as  $h^+$  or an  $\text{HO}^{\cdot}$  scavenger and therefore it needs an optimal concentration for the maximum degradation of MB.

The degradation pathway of MB can be arrived based on visible absorbance spectral change (Supplementary data, Fig. S2) and LC-MS spectral (Supplementary data, Fig. S3) observations. The observed blue shift (Supplementary data, Fig. S2) in absorption maximum of MB (665 nm) and the consequent removal of methyl groups via N-dealkylation<sup>11</sup> suggests that the degradation pathway proceeds via demethylation. The degradation pathway is summarized in Fig. 7 and is shown in Scheme 1.

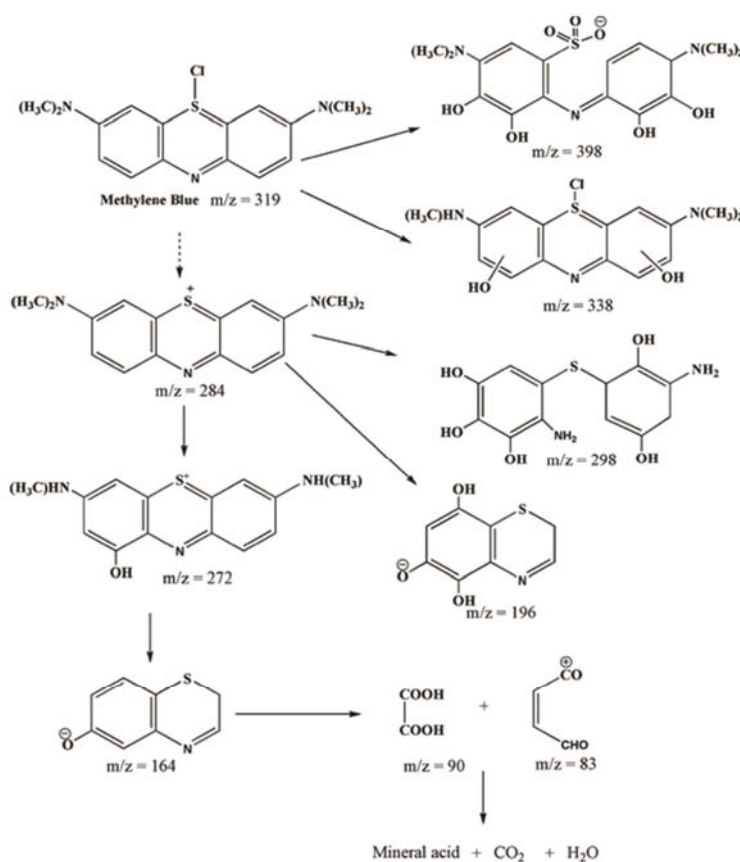


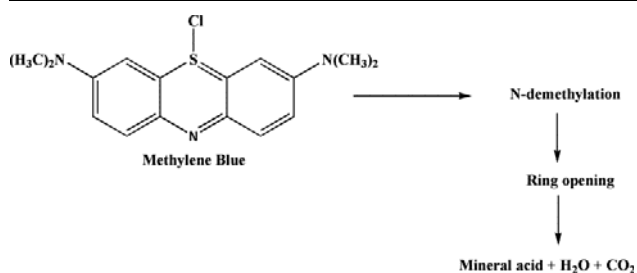
Fig. 7 — Degradation pathway of MB.



Table 4 — Comparison of degradation efficiencies of present and earlier reported catalysts

Catalyst <sup>a</sup>	Light source	Reaction cond.	% Degrad. and time	Ref.
Chit-Ppy-TiO <sub>2</sub> (250 mg/L)	150 W halogen lamp	pH = 6.9, [MB] = 50 mg/L, T = 25°C	96.5 in 2 h	This work
Fe/TiO <sub>2</sub> (1000 mg/L)	Sunlight	[MB] = 10 mg/L	84.9 in 6 h	[29]
Fe/TiO <sub>2</sub> -MWCNT (1000 mg/L)	8 W LED (visible) + ultra-sound (28 kHz)	[MB] = 50 mg/L, T = 25°C H <sub>2</sub> O <sub>2</sub> = 1.5 mM	~ 82 ~ 62 (without H <sub>2</sub> O <sub>2</sub> )	[30]
N-TiO <sub>2</sub> (1000 mg/L)	300 W xenon lamp	[MB] = 10 mg/L	92 in 1 h	[31]
ZnS-CdS (100 mg/L)	500 W halogen lamp	[MB] = 10 mg/L, T = 25°C	73 in 6 h	[32]
EBFTE/TiO <sub>2</sub> (15 mg)	450 W Hg lamp	[MB] = 0.1 mg/L	~ 95 in 160 min	[33]
ZnFe <sub>2</sub> O <sub>4</sub> /MWCNT (1000 mg/L)	160 W Hg lamp	[MB] = 10 mg/L, T = 25°C H <sub>2</sub> O <sub>2</sub> = 2 ml	99 in 5 h	[34]
Pd/TiO <sub>2</sub> Chitosan (1.5 g/L)	300 W Xenon lamp	[MB] = 75 mg/L, T = 25°C	99.5 in 30 min	[35]
POP/TiO <sub>2</sub> (6 g/L)	500 W xenon lamp	pH = 7.2, [MB] = 15.6 mg/L, T = 30°C	100 in 4 h	[36]
rGO/TiO <sub>2</sub> /ZnO (100 mg/L)	300 W xenon lamp	[MB] = 0.3 mg/L	92 in 2 h	[37]

<sup>a</sup>r-GO = reduced graphene oxide, POP = poly-*o*-phenylenediamine, EBFTE = (E)-1,2-bis(5-formyl-2-thienyl) ethylene.



Simplified schematic of degradation pathway of MB

### Scheme 1

#### Comparison of degradation efficiencies of present and reported catalysts

Table 4 presents a comparative account of degradation efficiencies of the present ternary Chit-Ppy-TiO<sub>2</sub> (1:1:100) catalyst and various other catalysts reported in literature<sup>29–37</sup>. The reaction condition and light source are not identical for the present and reported works and hence these are also given in Table 4. A rational comparison of these data shows that the present catalyst has better performance.

#### Conclusions

A three component organic-inorganic hybrid catalyst, Chit-Ppy-TiO<sub>2</sub> and two component TiO<sub>2</sub> hybrids with bio-polymer chitosan and conducting polymer (Ppy) are studied for the visible light degradation of MB. The ternary catalyst Chit-Ppy-TiO<sub>2</sub> (1:1:100) exhibits the highest activity towards degradation of MB among the synthesized catalysts. In the binary systems, the presence of Chit enhances the activity of TiO<sub>2</sub> by adsorbing more dye molecules, while the presence of Ppy enhances the efficiency of

TiO<sub>2</sub> via sensitization process. In the ternary system, the presence of both Chit and Ppy enhances the degradation ability of TiO<sub>2</sub> via combined effect of chitosan and Ppy. In addition, the catalyst is found to be stable even after four cycles. All these results together indicate that the designed three-component catalyst, Chit-Ppy-TiO<sub>2</sub>, in 1:1:100 weight proportion ratio has better photocatalytic functionality in visible region than the conventional bare TiO<sub>2</sub>. The ternary system can function as an efficient photocatalyst, both in lab-available visible light and naturally available sunlight. Thus we have successfully chemically modified TiO<sub>2</sub> to make it an efficient and visible light active photocatalyst.

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